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Short communication

Carbon—carbon bond forming reactions: Application of covalently anchored 2,4,6-triallyloxy-1,3,5-triazine (TAT) Pd(II) complex over modified surface of SBA-15 to Heck, Suzuki, Sonogashira and Hiyama cross coupling reactions

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Hiyama

ABSTRACT

A highly active SBA-15-TAT-Pd(II) catalyst was synthesized from organofunctionalized SBA-15 and 2,4,6-triallyloxy-1,3,5-triazine. The catalyst was employed in carrying out Heck, "copper-free" Sonogashira, Suzuki and Hiyama cross coupling reactions. Under the optimized conditions the catalyst displays excellent catalytic activity in delivering the desired products in good to excellent yields. The catalytic system exhibited superior activity regarding the time taken for the completion of reaction, isolation, Pd loading (0.62 mmol%) and yields of products as compared to the earlier reported heterogeneous SBA-15 anchored Pd catalysts. The catalyst could be recycled and reused for five times without any appreciable loss of catalytic activity.

1. Introduction

C—C bond forming reactions remain the most widely explored area in the field of synthetic organic chemistry. The palladium catalyzed cross coupling reactions form an important class of C—C bond forming reactions. The products obtained lead to important intermediates which have varied applications in the field of pharmaceuticals, natural product synthesis, material chemistry and many more [1]. Although homogeneous palladium catalysts involving the use of phosphine ligands have been dominating the area for quite some time, the field of heterogeneous catalysis in recent times has emerged an important area in the palladium catalyzed carbon—carbon bond forming reactions [2].

Over the past few years researchers have been successful in synthesizing various heterogeneous palladium catalysts. These include palladium complexes anchored to various inorganic or organic supports like Pd/SiO_2 [3], Pd/C [4], palladium/resin [5], palladium/MgO [6], Pd-montmorillonite [7], Pd/Al_2O_3 [8], palladium incorporated zeolites [9], SBA-15 supported palladium catalyst [10], and many others [11]. These catalysts tend to catalyze only one kind of cross coupling reaction most of the times. In recent times ordered mesoporous materials have been utilized as a solid support in the synthesis of heterogeneous catalysts. Among these materials SBA-15 has triggered the interests of various researchers due to its high thermal stability, high surface areas, ease of accessibility and uniform pores size. The SBA-15 has added advantage that it can be suitably modified to develop various catalysts by functionalizing the organic hydroxyl groups and further the covalent bonding with inorganic support prevents the leaching of active site.

As a part of our ongoing research program on the synthesis of SBA-15 supported heterogeneous catalyst [12] we have recently accomplished the synthesis and characterization of SBA-15-TAT-Pd(II) and its application for the hydrogenation of a variety of aromatic nitro and unsaturated compounds to their saturated counterparts [13]. The catalyst displayed high TON under low catalytic loading and the hydrogenation reaction was completed in shorter period of time. These attractive features of catalyst along with our interest in C—C bond forming reactions drew our attention in employing the catalyst in mainly palladium catalyzed cross-coupling reactions.

2. Result and discussion

2.1. Catalyst screening

The palladium catalyzed C—C bond forming reactions are the most widely used organic reaction for synthesis of various biaryl substituted compounds. Among these the major one are Heck, Suzuki, Sonogashira and Hiyama coupling reactions [14]. The Heck reaction involves formation of substituted styrenes (or substituted vinyl compounds) employing aryl

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iodides or triflates (or vinyl iodides/triflates) and activated alkene in the presence of base and palladium catalyst [15].

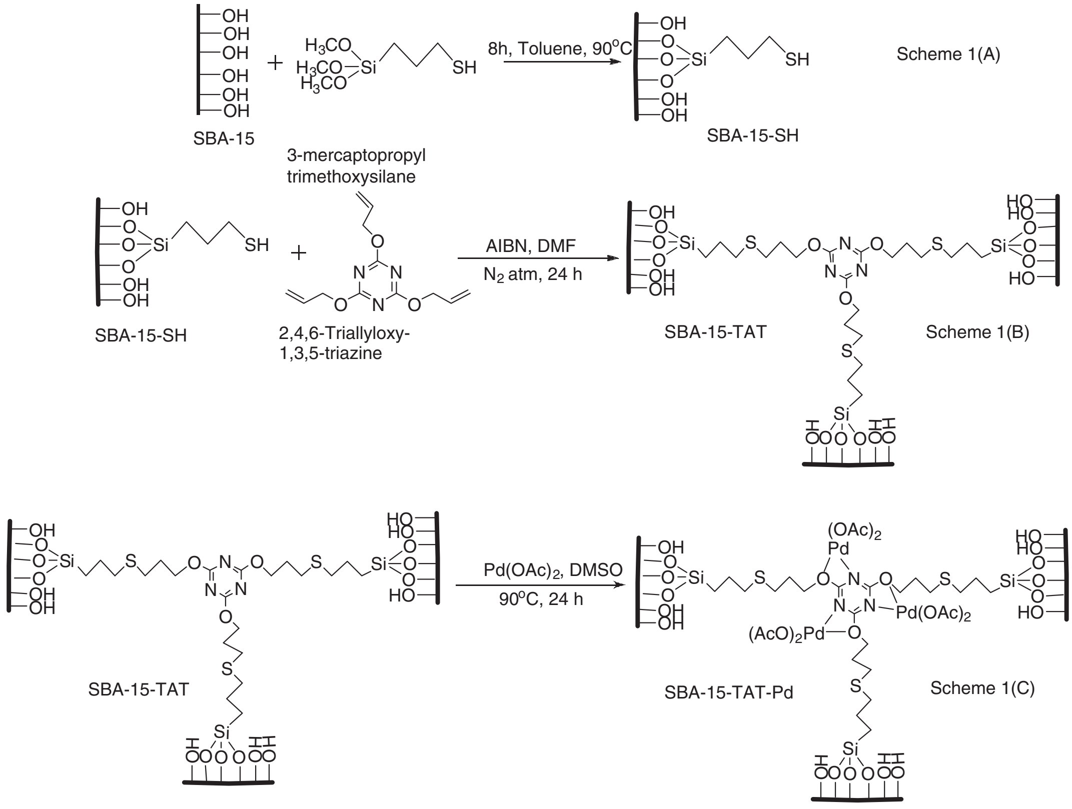
The Suzuki reaction employs aryl iodides and various phenyl boronic acids as coupling partners leading to formation of substituted biaryls [16]. In case of Sonogashira reaction various acetylenes are formed employing phenyl acetylenes and aryl iodides as coupling partners in the presence of base [17]. The Hiyama reaction also provides biaryls but it involves phenyltrimethoxysilanes and aryl iodide as the coupling partners [18]. A variety of modifications in the palladium catalyst involving both homogeneous and heterogeneous palladium catalyst has resulted in much broader range of acceptors and donors being amenable to these reactions. As a part of our keen interest in palladium catalyzed reactions we have explored the SBA-15-TAT-Pd(II) catalyst for its catalytic activity in the Heck, Suzuki, Sonogashira and Hiyama coupling reactions.

The synthesis of SBA-15-TAT-Pd(II) catalyst was carried out by the procedure described by Singh and Sharma [13]. The procedure involves stirring and refluxing a mixture of organofunctionalized SBA-15, 2,4,6-triallyloxy-1,3,5-triazine and azobisisobutyronitrile (AIBN) (initiator) in DMF at 100 °C for 24 h under nitrogen atmosphere. The solid obtained was filtered and purified by soxhlet extraction using DCM and then vacuum dried. For anchoring of palladium on triazine modified SBA-15, a solution of $Pd(OAc)_2$ and triazine modified SBA-15 in DMSO was stirred and resultant product was purified by washing with THF and soxhlet extraction using DCM (Scheme 1). The catalyst was well characterized for its texture, structure of mesoporous channel and other physicochemical properties using analytical techniques such as CP-OES, XRD, N_2 sorption measurement isotherm, TGA & DTA, solid state ^{13}C, ^{29}Si NMR spectroscopy, FT-IR, XPS, DRS UV–Visible, SEM and TEM [13].

We examined the catalytic activity of SBA-15-TAT-Pd(II) catalyst initially for Heck reaction using iodobenzene and ethyl acrylate. The reaction proceeded smoothly in 1 h to afford the desired product, ethyl cinnamate in 98% yield. Encouraged by this result we considered extending the application of the catalyst for other carbon—carbon bond forming reactions such as Suzuki, Sonogashira and Hiyama cross-coupling reactions. The reactivity of catalyst was investigated under the optimized conditions for the respective reactions (see Tables 1–4). To our delight the catalyst displayed excellent reactivity with a very low catalytic loading (0.62 mmol%) yielding the desired products in good to excellent yields.

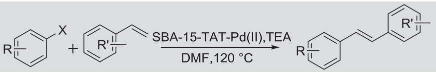
For the Heck coupling, the model reaction was carried using iodobenzene and ethyl acrylate as a starting materials using DMF as solvent and triethyl amine as base at 120 °C. Under this optimal reaction condition the reaction went smoothly to furnish desired product, ethyl cinnamate in excellent yield. To examine the scope of catalyst various substituted aryl iodides, acrylates and styrenes were also employed in the reaction under the optimized conditions. In case of aryl iodides the substituents showed little or no effect on the outcome of reactions. The reaction proceeded well with both the electron withdrawing and electron donating groups. Under the same reaction conditions we examined bromo benzene and chloro benzene for the Heck reaction. It was observed that the products were obtained in prolonged reaction time (24 h for bromobenzene and 30 h for chlorobenzene). In case of bromobenzene and chlorobenzene the electron withdrawing substituents produced an accelerating effect on the rate of reaction although the yields were found to be similar in both the cases. While studying the effect of substitution on other coupling partners i.e. styrenes and acrylates it was found that the catalyst works well with both electron withdrawing and electron donating substituents. Another interesting observation of these studies was that in case of α-methyl styrene the reaction took longer time for the completion (Table 1, entry 1o). This is probably due to the steric bulk of methyl group.

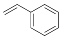
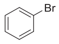
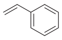
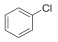
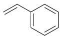
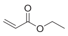
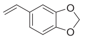
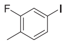
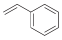
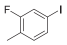
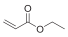
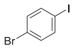
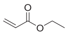
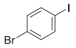
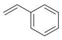
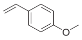
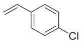
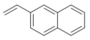
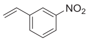
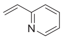
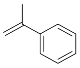
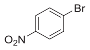
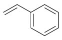
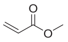
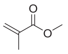
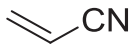
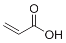
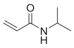
We then further investigated the compatibility of SBA-15-TAT-Pd(II) catalyst for Sonogashira reaction. The reaction was optimized using iodobenzene and phenylacetylene as coupling partners. To study the effect of CuI on Sonogashira reaction, the reaction was carried out both in presence and in absence of CuI. It was found that the CuI was required only when inorganic bases like K_2CO_3 were used for reaction. When triethyl amine was used as a base in reaction the desired product was



Scheme 1. Synthesis of SBA-15-TAT-Pd(II) catalyst.

Table 1
Heck reaction of various aryl iodides with different olefin.[a]

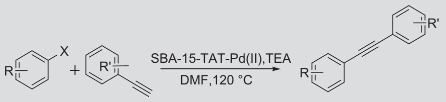


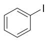
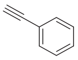
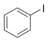
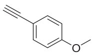
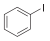
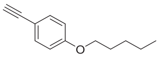
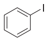
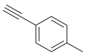
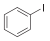
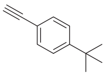
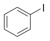
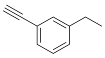
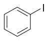
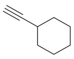
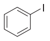
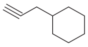
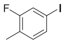
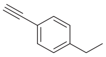
Aryl iodide	Olefin	Entry	Yield[b] (%)	Time (h)
		1a	95	1
		1b	92	24
		1c	90	30
		1d	95	1
		1e	90	1
		1f	87	1
		1g	85	1
		1h	85	1
		1i	90	1
		1j	85	1
		1k	90	1
		1l	90	1
		1m	80	1
		1n	75	2
		1o	80	6
		1p	75	4
		1q	80	1
		1r	70	1
		1s	75	1
		1t	70	1
		1u	70	2

[a] Reaction conditions: Aryl halide (1 mmol), styrene (1.15 mmol), TEA (3 mmol), DMF (3.5 mL), heterogeneous SBA-15-TAT-Pd(II) catalyst (0.62 mmol% Pd). Temperature = 120 °C.

[b] Isolated yields, product analyzed by GCMS and ^{1}H, ^{13}C NMR spectroscopy.

Table 2
Sonogashira reaction of various aryl iodides with different phenyl acetylene.[a]



Aryl iodide	Phenyl acetylene	Entry	Yield[b] (%)	Time (h)
		2a	90	1
		2b	85	1
		2c	82	1
		2d	86	1
		2e	87	1
		2f	90	1
		2g	80[c]	3
		2h	80[c]	3
		2i	80	1

[a] Reaction conditions: Aryl halide (1 mmol), phenyl acetylene (1.15 mmol), TEA (3 mmol), DMF (3.5 mL), heterogeneous SBA-15-TAT-Pd(II) catalyst (0.62 mmol% Pd). Temperature = 120 °C.

[b] Isolated yields, product analyzed by GCMS and ^{1}H, ^{13}C NMR spectroscopy.

[c] CuI (5 mol%) was used.

obtained even in absence of CuI. Based on this observation we proceeded ahead to carry out Sonogashira reaction of various aryl iodides and substituted phenyl acetylenes in presence of NEt_3 as base. As in the case of Heck the SBA-15-TAT-Pd(II) catalyst showed tolerance for wide range of substituents furnishing desired product in moderate to high yields (see Table 2). In case of aliphatic acetylenes the presence of CuI was essential for the progress of reaction.

Since we were successful in employing SBA-15-TAT-Pd(II) catalyst in Heck and Sonogashira reaction we now further considered investigating the performance of catalyst in case of Suzuki (Table 3) and Hiyama (Table 4) coupling reactions.

The model reaction was performed using iodobenzene and phenyl boronic acid as starting material DMF as solvent and K_2CO_3 as the base. The reaction proceeded smoothly to afford the desired product in excellent yield. In order to extend the substrate scope the reaction was performed with other substituted aryl iodides and phenylboronic acids under the optimized conditions. The results obtained were similar as in case of Heck and Sonogashira coupling reactions. Thus from the results obtained the catalyst was found to be highly active for the above mentioned reactions and exhibited superior activity regarding the time taken for the completion of reaction, isolation, Pd loading and yields of products as compared to the earlier reported heterogeneous SBA-15 anchored Pd catalysts [19,20].

Furthermore to test the practical utilization of catalyst in gram scale, reaction was carried out using 1 g of phenyl iodide and styrene under the optimal condition for 1 mmol scale for Heck reaction. The reaction proceeded smoothly in 4 h yielding trans-stilbene in 80% yield. The result obtained proves that the catalyst can be easily utilized for performing large scale reactions.

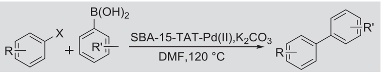
2.2. Study for heterogeneity of SBA-15-TAT-Pd(II) catalyst

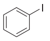
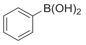
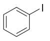
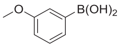
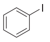
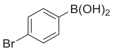
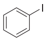
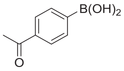
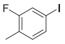
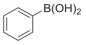
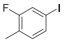
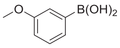
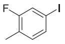
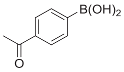
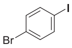
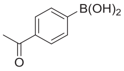
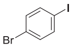
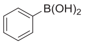
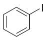
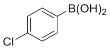
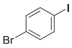
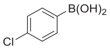
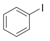
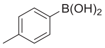
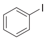
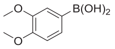
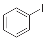
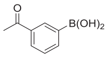
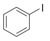
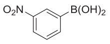
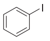
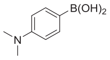
To test if metal was leached out from the solid catalyst during reaction; the hot filtration test was performed with Heck reaction under optimized reaction conditions; styrene (1.15 mmol, 0.1197 g), iodobenzene (1 mmol, 0.204 g), triethyl amine base (3 mmol, 0.3035 g), DMF 3.5 mL, heterogeneous SBA-15-TAT-Pd(II) catalyst (30 mg), reaction temperature 120 °C. The Heck coupling reaction mixture was collected by filtration at the reaction temperature (120 °C) after a reaction time of 30 min which gave 58% conversion of iodobenzene. The supernatant solution obtained after filtration from the reaction mixture containing SBA-15-TAT-Pd(II) catalyst at the elevated reaction temperature (120 °C) (in order to avoid possible reco-ordination or precipitation of soluble palladium upon cooling) did not show any further progress in reaction. Thus ICP-AES results of the hot filtration test suggested that Pd was not leached out from the solid catalyst during the coupling reaction confirming that the palladium catalyst remains on the support even at elevated temperature during the reaction.

2.3. Recycling of catalyst

The catalyst was then further screened for its recyclability and reusability. The catalyst was easily recovered through simple vacuum filtration over Whatman filter paper. The catalyst after washing with ethyl acetate and drying in oven was subjected for the use in next reaction.

Table 3
Suzuki reaction of various aryl iodides with different phenyl boronic acids.[a]



Aryl iodide	Phenyl boronic acids	Entry	Yield[b] (%)	Time (h)
		3a	90	1
		3b	90	1
		3c	85	1
		3d	82	1
		3e	80	1
		3f	85	1
		3g	85	1
		3h	85	1
		3i	85	1
		3j	85	1
		3k	85	2
		3l	85	1
		3m	80	1
		3n	87	1
		3o	82	1
		3p	86	2

[a] Reaction conditions: Aryl halide (1 mmol), phenyl boronic acid (1.15 mmol), K_2CO_3 (3 mmol), DMF (3.5 mL), heterogeneous SBA-15-TAT-Pd(II) catalyst (0.62 mmol% Pd). Temperature = 120 °C.

[b] Isolated yields, product analyzed by GCMS and ^1H, ^{13}C NMR spectroscopy.

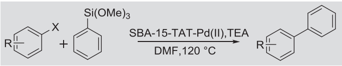
The catalyst showed no loss of activity and can be reused (up to five times). Fig. 1 shows the effect of recycling of catalyst in the Heck reaction on the yields of desired products. The yields of the product obtained by using fresh SBA-15-TAT-Pd(II) catalyst and those obtained from using spent SBA-15-TAT-Pd(II) catalyst are comparable.

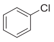
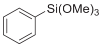
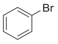
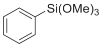
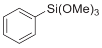
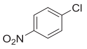
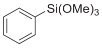
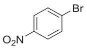
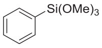
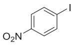
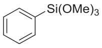
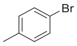
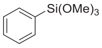
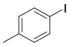
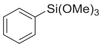
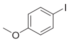
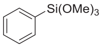
For further confirmation, XPS analyses of fresh SBA-15-TAT-Pd(II) and spent SBA-15-TAT-Pd(II) catalyst (five recycles) have been carried out to probe the change in the oxidation state of palladium in its coordination sphere (Fig. 2). The XPS spectrum of the recycled catalyst clearly shows the presence of peaks at 337.5 eV and 342.6, corresponding to 3d5/2 and 3d3/2 respectively, of Pd(II) species. The absence of peaks at 335.6 eV and 340.7 eV, corresponding to Pd(0) moiety further confirms the absence of Pd(0) moiety. Even after repeated cycles of the Heck reaction, catalyst SBA-15-TAT-Pd(II) shows the same Pd 3d peaks (Fig. 2) (spent and fresh catalyst), suggesting that the oxidation state of the immobilized Pd did not change after repeated reactions.

3. Conclusions

Covalently anchored 2,4,6-triallyloxy-1,3,5-triazine (TAT) Pd(II) complex over modified surface of SBA-15 was synthesized and tested for its catalytic activity in Heck, Suzuki, Sonogashira and Hiyama cross coupling reactions. Under the optimized conditions the catalyst displayed excellent catalytic activity in delivering the desired products in good to excellent yields. An important feature of SBA-15-TAT-Pd(II) catalytic system is its application in the “copper-free” Sonogashira cross coupling reaction. The reaction yielded desired product without use of copper(I) iodide when phenyl acetylenes were used as coupling partners (although copper iodide was required for aliphatic acetylenes). The catalytic system exhibited superior activity regarding the time taken for the completion of reaction, isolation, Pd loading (0.62 mmol%) and yields of products as compared to the earlier reported heterogeneous SBA-15 anchored Pd catalysts [19,20].

Table 4
Hiyama reaction of various aryl iodides with phenyl trimethoxysilane.[a]



Aryl iodide	Phenyl trimethoxysilane	Entry	Yield[b] (%)	Time (h)
		3a	29	12
		3a	83	8
		3a	98	3
		4a	98	1
		4a	99	2
		4a	99	1
		3i	96	5
		3l	94	4
		4b	89	5

[a] Reaction conditions: Aryl halide (1 mmol), phenyl trimethoxysilane (1.5 mmoL), TEA (3 mmol), DMF (3.5 mL), heterogeneous SBA-15-TAT-Pd(II) catalyst (0.62 mmol% Pd). Temperature = 120 °C.

[b] Isolated yields, product analyzed by GCMS and ^1H, ^{13}C NMR spectroscopy.

Acknowledgments

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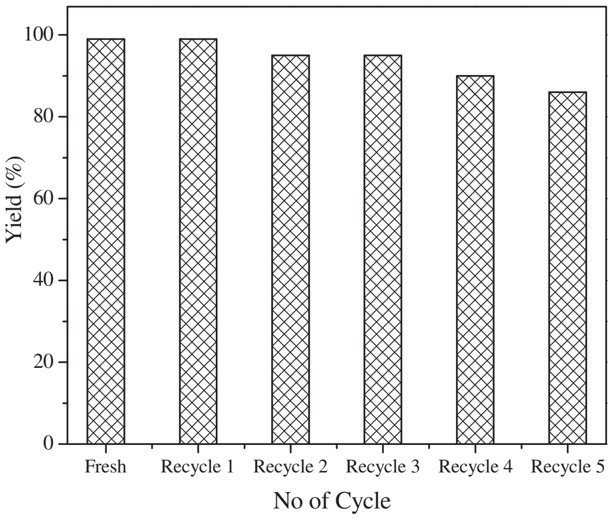

Fig. 1. Recycling study of heterogeneous catalyst SBA-15-TAT-Pd(II) for Heck reaction.

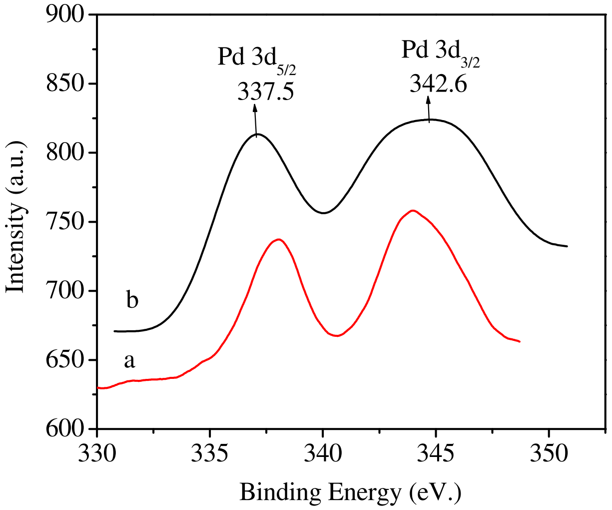

Fig. 2. XPS spectra of SBA-15-TAT-Pd(II). (a) Fresh catalyst, (b) spent catalyst.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.05.013.

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