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Efficient Suzuki reaction catalyzed by recyclable clay carbapalladacycle nanocomposite in ionic liquid media

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ABSTRACT

In this Letter, we report the efficient recyclability and recoverability of ionic tagged carbapalladacycle and its hybrid MMT clay-nanocomposite catalyst in ionic liquid media $[TMBA]NTf_2$ for the Suzuki reaction. It has several distinct advantages which include the use of low levels of catalyst concentration, formation of desired products in high yields and good selectivity using chloro, bromo and iodo substituted aryl halides, and negligible formation of homo coupling products.

1. Introduction

Palladium catalyzed Suzuki cross coupling reaction of aryl halides with aryl boronic acids or esters is an important carbon–carbon bond formation reaction for the synthesis of substituted biaryls.[1–4] The substituted biaryl moiety is present in many pharmaceutically active compounds, herbicides, polymers, new materials, liquid crystals and ligands[5] to mention a few. Over the decades, several homogenous palladium based catalysts have been developed and reported in the literature to promote the Suzuki reaction.[6,7] Among these, Najera et al.[8] have developed oxime based palladacycle catalysts having unique properties of being thermally robust, air and moisture insensitive and avoid the use of phosphine ligands which get oxidized during the reaction. However, despite the various advantages associated with these catalysts, difficulties are encountered with regard to their separation and recoverability in the reaction process.

Further, based on the preference of the chemical industry and in the context of green chemistry, the heterogenization of an active homogenous catalyst is of interest for improved recyclability and recoverability, wherein the catalyst has both an expensive metal and ligand incorporated in it.[9] In the past, this heterogenization has been achieved by covalent or ionic immobilization on inorganic support materials such as clays,[10] silica,[11] zeolites,[12] polymers[13] and most recently, using ionic[14,15] and florous tags[16,17] to mention a few. Among these, Montmorillonite clay, an inexpensive and naturally occurring material, can act as an excellent host to active homogenous catalysts by ion exchange due to its smectite structure and two dimensional lamellar form.[18] This ionic immobilization results in the formation of a stable organic–inorganic hybrid catalytic system, particularly for metal and metal–ligand complex based catalysts.[19]

The reaction medium used in any reaction is also of great significance and in particular, the use of benign reaction medium such as water[20,21] and ionic liquids[22,23] has proven to be excellent substitutes to the previously used high boiling solvents, such as DMF in the Suzuki reaction.[24]

In continuation to our ongoing research program on the development of new recyclable and recoverable heterogeneous catalysts based on ionic liquids[25] and solid supports,[26,27] we had previously developed a clay based carbapalladacycle nanocomposite catalyst and successfully carried out the Heck and Sonogashira reaction.[28] Encouraged by our previous results, we have expanded the application of ammonium tagged oxime carbapalladacycle (**1**) and its clay nanocomposite (**2**) as shown in Figure 1, for executing Suzuki reaction in ionic liquid media. The reaction was also tried in aqueous medium but lower yields (65% for model reaction) were obtained. Recyclability of the catalyst has also been carried out upto seven cycles.

The IR, NMR, and mass spectral data of catalysts (**1**) and (**2**) were comparable with those reported in the literature.

The optimization of reaction conditions for model Suzuki reaction as shown in Scheme 1, has been done with respect to catalyst

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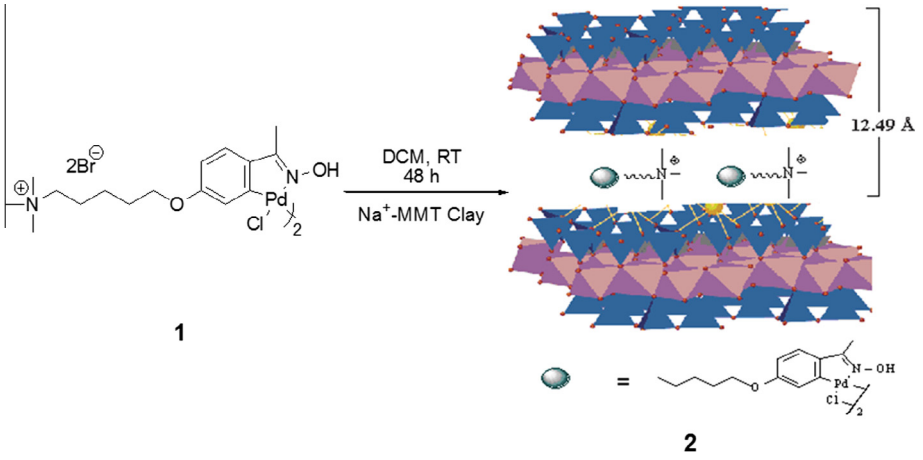
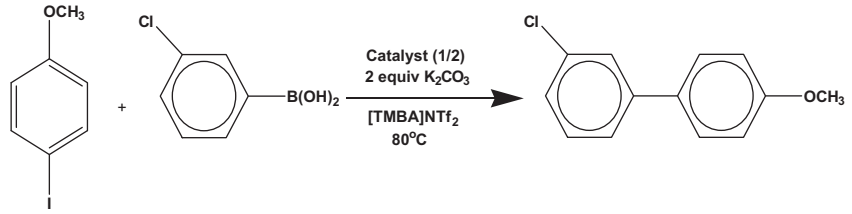


Figure 1. Ammonium tagged oxime carbapalladacycle (**1**) and its clay nanocomposite (**2**).



Scheme 1. General scheme for the model Suzuki reaction using catalyst (**1**) and (**2**).

concentration, temperature, reaction time, base and ionic liquid/aqueous media used in the reaction.

Initial assessment of the catalyst (**1**) was done by optimization of catalyst loading, time, and temperature of reaction between 4-iodoanisole and 3-chlorophenylboronic acid as the model reaction with Na_2CO_3 and [TMBA]NTf_2 [tetramethyl butyl ammonium bis (trifluoromethanesulfonyl) imide] as the base and solvent respectively as shown in Table 1. In the reaction carried out over a time period of 12 h, the catalyst concentration was varied from 0.05 mol % to 0.006 mol % (entries 1–4). The lowest concentration of catalyst at which maximum yield was obtained was found to be 0.012 mol % (entry 3). The effect of time of reaction was also studied by reducing it to 6 h for catalyst concentration of 0.025 mol % (entry 5) and 0.012 mol % (entry 6), but a lower yield of 73% and 55%, respectively of the desired product was obtained. Further lowering of reaction temperature to 60 °C resulted in a decrease in yield to 62% (entry 7). Accordingly, a precatalyst loading of 0.012 mol % of Pd was used at 80 °C for 12 h for our subsequent experiments as the optimized reaction conditions.

Further, it is known that nature of base is also a very important factor for determining the efficiency of the Suzuki cross-coupling reaction.[29–31] Therefore, the influence of various organic and inorganic bases was investigated for Suzuki coupling reaction of 4-iodoanisole and 3-chlorophenylboronic acid in [TMBA]NTf_2 and the results are summarized in Table 2. The results show that Na_2CO_3 (Table 2, entry 1) is the best choice as compared to the other bases.

We also explored the possibility of carrying out the model Suzuki reaction with catalyst (**1**) in water as the reaction media under optimized reaction conditions. The desired biaryl product was obtained in a lower GC–MS yield of 65.87% and the recoverability of the catalyst from the aqueous media also posed a problem.

Under the optimized conditions, as determined for catalysts (**1**) (Pd content 2.39 mmol/1 g of clay as determined by AAS), the reaction was also carried out with catalyst (**2**) (Pd content 1.178 mmol/1 g of clay as determined by AAS) and both the catalysts were further employed for the Suzuki reaction with various phenylboronic acids using 4-iodoanisole and 4-bromoanisole as illustrated in

Table 1
Effect of catalyst loading, time, and temperature on Suzuki reaction[a]

Entry (mol % of Pd)	Catalyst	Time (h)	Temp (°C)	Yield[b] (%)
1	0.05	12	80	98
2	0.025	12	80	97
3	0.012	12	80	96
4	0.006	12	80	47
5	0.025	6	80	73
6	0.012	6	80	55
7	0.012	12	60	62

[a] Reaction condition: 4-iodoanisole (0.1 g, 1 mmol), 3-chlorophenylboronic acid (0.1 g, 1.5 mmol), catalyst (**1**), Na_2CO_3 (2 mmol), TMBA]NTf_2 (0.5 ml).
[b] Isolated yield.

Table 2
Effect of base on Suzuki reaction[a]

Entry	Base	Yield[b] (%)
1	Na_2CO_3	96
2	$CH_3COONa{\cdot}3H_2O$	30
3	Et_3N	67
4	Morpholine	44
5	K_2CO_3	75
6	$Na_3PO_4{\cdot}12H_2O$	83

[a] Reaction condition: 4-iodoanisole (0.1 g, 1 mmol), 3-chlorophenylboronic acid (0.1 g, 1.5 mmol), catalyst (**1**) (0.012 mol % of Pd), Base (2 mmol), TMBA]NTf_2 (0.5 ml), 80 °C, 12 h.
[b] Isolated yield.

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