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Green conditions for the Suzuki reaction using microwave irradiation and a new HNT-supported ionic liquid-like phase (HNT-SILLP) catalyst

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A new catalytic system based on modified halloysite nanotubes was employed in the Suzuki reaction under microwave irradiation. A set of solvents, times and bases was screened and the best experimental conditions were obtained when the reactions were carried out for 10 min in water–ethanol at 120 °C in presence of K_2CO_3 as base. Good recyclability was observed. The new catalytic system was employed using either 1 mol% or 0.1 mol%. The palladium catalyst displayed good activity, allowing the synthesis of several biphenyl compounds in high yield working with only 0.1 mol% palladium loading. The application of microwave irradiation decreased the reaction time and also improved conversion with respect to traditional heating. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: Halloysite; Suzuki reaction; microwave; SILLP (supported ionic liquid-like phase)

Introduction

In the history of organic chemistry, the formation of new bonds between two carbon atoms has always been one of the fundamental reactions,[1] and therefore much research around the world has tried to broaden new methodologies that are able to improve the reaction conditions.

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids[2] is one of the most valuable synthetic routes for the preparation of symmetric and asymmetric biaryls, which are important skeletons in the structures of biologically active compounds,[3] agrochemicals, pharmaceuticals,[4] polymers,[5] ligands[6] and functional materials.[7] The key advantages of the Suzuki–Miyaura cross-coupling are: (i) the mild conditions under which it is conducted; (ii) the high tolerance toward functional groups, (iii) the commercial availability and stability of boronic acids to heat, oxygen and water; and (iv) the ease of handling and separation of boron-containing by-products from the reaction mixtures.[8]

Usually, the Suzuki reaction is performed under homogeneous conditions in the presence of trivalent phosphine ligands[9] or in the presence of *N*-heterocyclic carbenes (NHCs)[10] or with palladacycle complexes.[11] To avoid problems related to separation of homogeneous catalysts, palladium complexes or nanoparticles were immobilized on various supports such as silica, alumina, zeolites, organic polymers, magnetic nanoparticles and dendrimers.[12]

In addition, Suzuki reactions were also carried out in supported ionic liquid-like phase (SILLP) – structured materials able to present most characteristics and properties of ionic liquids as molecular solvent, playing an active role in the immobilization and stabilization of Pd species.[13]

Among various inorganic supports for immobilizing palladium catalysts, silica is very promising because of its high surface area, good thermal stability, ready availability and economic viability, and relatively easy covalent modification with organic or organometallic moieties.

In this area, emerging materials with an appealing perspective for application in catalysis are halloysite nanotubes (HNTs). Halloysite is a double-layered aluminosilicate mineral that has a predominantly hollow tubular structure.

The functionalization of HNTs is a good strategy for introducing an organic moiety on to the external surface and therefore to obtain innovative catalyst supports as demonstrated for metalloporphyrin[14] immobilization and heterogeneous atom transfer polymerization of methyl methacrylate (MMA) into poly (methyl methacrylate) (PMMA) using CuBr as catalyst.[15] HNTs have also been used as a catalyst support for platinum in the synthesis of allyl-ended hyperbranched organic silicone resins.[16]

Similar to recoverable catalysts, microwave-promoted synthesis is also an area of increasing interest in both academic and industrial laboratories since microwaves are an efficient and non-polluting mode of heating the reaction mixture.[17] The combination of microwave technology and heterogeneous

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catalysis is therefore likely to have a great impact on sustainable chemistry, and prove to be a better catalytic system from both economic and environmental viewpoints.

The Suzuki reaction has been successfully carried out using water as reaction medium in conjunction with microwave heating;[18] furthermore, the addition of an ionic liquid to the reaction mixture as co-solvent has led to very high conversions and clean reactions.[19]

Recently,[20] we modified the external surface of halloysite nanotube with octylimidazolium moieties (HNT-IL) by microwave irradiation under solvent-free conditions. In the best synthesis the degree of loading of HNT, as estimated by TGA, was $0.15\,\text{mmol}\,\text{g}^{-1}$. The preparation of supported palladium nanoparticles (HNT-IL/Pd), where the metal catalyst can be linked by electrostatic interactions in the HNT-IL support, was achieved by anion exchange from Br^- to $PdCl_4^{2-}$ (aqueous solution of Na_2PdCl_4). The solid material, HNT-IL/($PdCl_4^{2-}$), was recovered by filtration and, finally, the Pd(II) was reduced to Pd^0 with $NaBH_4$ in ethanol. Following this procedure, an HNT-IL/Pd catalyst with 0.7 wt% Pd was obtained, as determined by energy-dispersive X-ray measurement (Fig. 1). Preliminary studies have confirmed the good catalytic activity of HNT-IL/Pd support employed in the Suzuki reaction using H_2O/EtOH (1:1) as solvent, at 50 °C in the presence of K_2CO_3 for 19 h.

It is known that ceramic materials based on aluminosilicates react quickly under microwave irradiation with consequent rapidity and uniformity of heating;[21] therefore, in this work, we have investigated our catalytic system for the Suzuki reaction between phenylboronic acid and several aryl halides under microwave irradiation.

Results and Discussion

The Suzuki cross-coupling reaction between several aryl halides and phenylboronic acid in the presence of HNT-IL/Pd catalyst was investigated under microwave irradiation. Our studies were focused on determining the influence of different reaction parameters such as the reaction time, solvent, base and amount of catalyst.

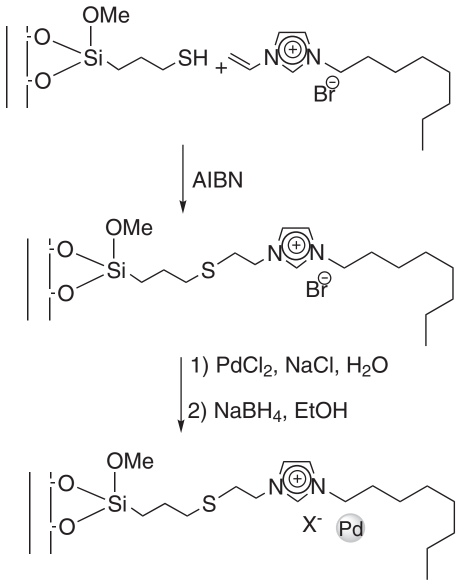


Figure 1. Synthesis of HNT-Pd catalyst.

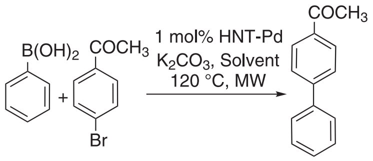
First, it is interesting to note that the catalyst HNT-IL/Pd previously obtained[20] is a material with lower Pd loading (0.7 wt%) compared to the silica-modified support (10 wt%);[22] this is a consequence of the different degree of IL loading on HNT as compared to silica, which has a greater surface area.

Table 1 shows the effect of different solvents on the Suzuki coupling between phenylboronic acid and 4-bromoacetophenone that was selected as model. We have used polar and non-polar solvents with different abilities to convert electromagnetic energy into heat, with an irradiation time of 2, 6 and 10 min, respectively, at a temperature of 120 °C. This value was chosen according to literature conditions.[23]

As reported in the literature,[18] water as solvent is central to the success of the reaction (entries 7 and 14); in our case the best conditions were obtained when we used as solvent the mixture H_2O–EtOH (1:1) (entries 6 and 13), probably because it better dissolves both organic reagents and inorganic base. The best result was obtained using a reaction time of 10 min (entry 15); longer times of irradiation led to the degradation of compounds.

For further investigations we decided to use an ethanol–water mixture and an irradiation time of 10 min (entry 15). In order to investigate the role of the base, two bases were used, namely K_2CO_3 and Cs_2CO_3. The results show that K_2CO_3 was the optimum base under microwave irradiation at 120 °C in the presence of 1 mol% catalyst (Table 2, entries 1 and 3). As both metal

Table 1. Optimization of solvent and time for Suzuki cross-coupling reaction under microwave irradiation[a]

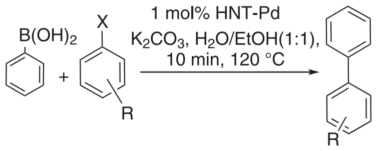


Entry	Solvent	Time (min)	Conversion (%)[b]
1	THF	2	Trace
2	MeOH	2	12
3	EtOH	2	24
4	Acetonitrile	2	—
5	DMF	2	—
6	H_2O/EtOH (1:1)	2	37
7	H_2O	2	30
8	THF	6	9
9	MeOH	6	10
10	EtOH	6	48
11	Acetonitrile	6	5
12	DMF	6	—
13	H_2O/EtOH (1:1)	6	55
14	H_2O	6	42
15	H_2O/EtOH (1:1)	10	>99

[a] Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.12 mmol), solvent (1.2 ml), HNT-IL/Pd (1 mol %). MW, microwave.

[b] Determined by ^1H NMR.

Table 2. Optimization of base for Suzuki cross-coupling reaction under microwave irradiation[a]



Entry	Ar-X	Base	Conversion (%)[b]
1	4-Bromoacetophenone	K_2CO_3	>99
2	4-Bromoacetophenone	Cs_2CO_3	71
3	4-Bromobenzaldehyde	K_2CO_3	>99
4	4-Bromobenzaldehyde	Cs_2CO_3	87

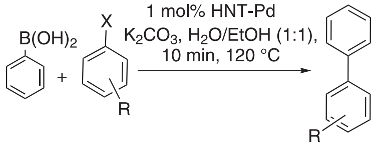
[a] Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), base (1.12 mmol), solvent (1.2 ml), HNT-IL/Pd (1 mol%).

[b] Determined by ^{1}H-NMR.

carbonates screened have similar basicity, the results suggest that there may be a cationic effect in the reaction.

In Table 3 are shown the data obtained using the catalytic system for Suzuki cross-coupling reaction of different types of aryl bromides, iodides and less reactive aryl chlorides, using phenylboronic acid under microwave irradiation at 120 °C in the presence of K_2CO_3; HNT-IL/Pd catalyst was used at 1 mol% and all reactions were run for 10 min.

Table 3. Suzuki cross-coupling reaction of phenylboronic acid with various halides under optimized reaction conditions under microwave irradiation[a]



Entry	Ar-X	Conversion (%)[b]
1	4-Bromoacetophenone	>99
2	3-Bromoacetophenone	80
3	4-Bromobenzaldehyde	>99
4	3-Bromobenzaldehyde	>99
5	4-Bromoanisole	>99
6	3-Bromoanisole	90
7	4-Bromotoluene	>99
8	2-Bromotoluene	>99
9	4-Bromoaniline	78
10	2-Bromobenzonitrile	>99
11	3,5-Bis(trifluoromethyl)bromobenzene	>99
12	1-Bromo-2,4,6-triisopropylbenzene	<5
13	1-Bromo 4-nitrobenzene	>99
14	4-Iodoacetophenone	>99
15	4-Iodotoluene	>99
16	Methyl 4-iodobenzoate	>99
17	2-Chlorobenzaldehyde	14
18	4-Chlorobenzaldehyde	33

[a] Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.12 mmol), solvent (1.2 mL), HNT-IL/Pd (1 mol%).

[b] Determined by ^{1}H-NMR.

Conversions were high, ranging from 78% to 100%; in all case no byproducts were detected and the conversions reported in Table 3 correspond to yields. Full conversions were achieved when aryl bromides and iodides were employed (entries 1, 3–5, 7, 8, 10, 11, 13 and 14–16 respectively), while less reactive aryl chlorides (entries 17 and 18) gave lower yields. However, it is noteworthy that in the latter cases no product was detected by traditional heating.

The Suzuki reaction was performed by aryl halides bearing both electron-donating and electron-withdrawing substituents and the results were comparable. Therefore, under the defined conditions, reactions did not show any sensitivity to electronic effects; for example, 4-bromoanisole or 4-bromotoluene (or 4-iodotoluene) have a comparable result to 4-bromobenzaldehyde (Table 3, entries 5, 7, 15, 3).

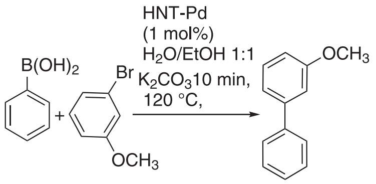
The data in Table 3 show that application of microwave irradiation can decrease the completion time of reaction and also improve conversions which respect traditional heating, as previously reported by our group (50 °C, 19 h).[20]

The introduction of a small amount of ionic liquid onto the HNT external surface was probably enough to obtain a dramatic change in the heating profiles by changing the overall dielectric properties of the reaction mixture, which consequently led to improved yields.

Catalyst Recycling

Recycling investigations were carried out using catalyst HNT-IL/Pd at 1 mol% in the reaction between phenylboronic acid and 3-bromoanisole (Table 4). The heterogeneous support allows efficient recycling by filtration. Indeed, the catalyst was reused for several cycles, and after each run the reaction mixture was centrifuged and the liquid mixture was decanted. The residual solid catalyst was employed again with fresh solvent, substrates and base. The HNT-IL/Pd catalyst could be reused for

Table 4. Recycling investigations[a]

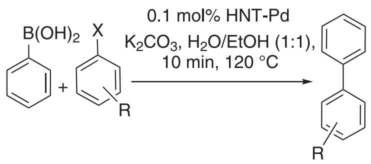


Entry	Cycle	Conversion (%)[b]
1	1	90
2	2	90
3	3	88
4	4	88
5	5	88

[a] Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.12 mmol), solvent (1.2 ml), HNT-IL/Pd (1 mol%).

[b] Determined by ^{1}H-NMR.

Table 5. Suzuki cross-coupling reaction of phenylboronic acid with various halides under optimized reaction conditions under microwave irradiation[a]



Entry	Ar-X	Conversion (%)[b]
1	4-Bromoacetophenone	>99
2	4-Bromobenzaldehyde	>99
3	3-Bromoanisole	90

[a]Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.12 mmol), solvent (1.2 ml), HNT-IL/Pd (1 mol%).
[b]Determined by ^{1}H-NMR.

five cycles while retaining the same activity and selectivity as well as without, presumably, loss of the active Pd species. It is known that when the SILLP/Pd catalyst was employed at high temperature no leaching of the catalyst was detected upon recycling.[24]

The absence of leaching in Pd catalysts immobilized on to gel-supported ionic-liquid phase has been ascribed to a 'release and catch' mechanism.[25] It has been proposed that during Suzuki coupling palladium is dissolved in solution (leaching), then after completion of the process palladium is redeposited on to the support and its full and efficient recovery can be achieved if the redeposition is complete at the end of the reaction.[25c] As can be seen in Table 4, the reaction yield ranged from 90% to 88%. We can therefore conclude that microwave irradiation did not destroy the HNT-Pd catalyst.

In order to use more green conditions, we checked if a lesser quantity of HNT-IL/Pd catalyst could be employed without affecting the yield, as well as the selectivity of the reaction. With this idea in mind, we carried out a set of reactions using catalyst HNT-IL/Pd in 0.1 mol% (Table 5). It is interesting to note that yields were comparable to those obtained using HNT-IL/Pd in 1 mol%. These results represent, in our opinion, a clear advantage because it is possible to employ only a small amount of heterogeneous catalytic material (5 mg).

Conclusions

In this work we have reported data on the Suzuki reaction in heterogeneous phase using as catalyst a new HNT-supported ionic liquid-like phase (HNT-SILLP) and microwave irradiation. The contributions of solvent, time, base and catalyst amounts were investigated. The results show that microwave irradiation improves yield and conversion in the Suzuki reaction in comparison to the traditional heating previously reported by our group. In addition, it is remarkable to note that the HNT-IL/Pd catalyst (support 1 mol%, Pd 7×10^{-3} mg) appears to be more efficient than those we used previously on a silica support (support 1 mol%, Pd 0.10 mg) despite lesser amounts of Pd on its surface. This latter aspect, with only a small amount of Pd used as the catalyst, associated with the advantages that microwave irradiation brought to the Suzuki reaction, in terms of energy saving, time and yield, contributes to a more efficient green process with less waste production. Recycling studies were briefly investigated, and HNT-SILLP showed good recyclability in such catalytic systems.

Experimental

General Data

Microwave-assisted syntheses were carried out with a CEM DISCOVER monomode system in a closed vessel. ^{1}H NMR spectra were recorded at 250 MHz in $CDCl_3$ solution at room temperature on a Bruker AC-E Series 300 spectrometer. Palladium chloride, aryl halide and all other chemicals were purchased from Sigma-Aldrich and used without further purification. HNT-Pd catalyst was synthesized according to published methods.[20]

Typical Procedure for the Suzuki Reaction via microwave irradiation

HNT-Pd catalyst (1% or 0.1 mol%), phenylboronic acid (65 mg, 0.547 mmol), K_2CO_3 (84 mg, 0.615 mmol), aryl bromide (0.55 mmol), ethanol (0.6 ml) and water (0.6 ml) were placed in a microwave test tube provided with a cap The mixture was inserted into microwave apparatus at a temperature of 120 °C and 14 W power, under constant stirring for 10 min; the solvent was then removed under reduced pressure and the residue was checked by ^{1}H-NMR to calculate conversion.

Recyclability of the Catalyst

HNT-IL/Pd catalyst (1 mol%), phenylboronic acid (65 mg, 0.547 mmol), K_2CO_3 (84 mg, 0.615 mmol), 3-bromoanisole (0.55 mmol), ethanol (0.6 ml) and water (0.6 ml) were placed in a microwave test tube provided with a cap. The mixture was inserted into the MW apparatus at a temperature of 120 °C and 14 W power, under constant stirring for 10 min. The reaction mixture was then centrifuged and the liquid mixture was decanted; the residual solid was washed with CH_2Cl_2, water and Et_2O. HNT-IL/Pd was dried and reused.

Acknowledgments

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