Accepted Manuscript

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PII:	\$1381-1169(15)30019-4
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2015.07.008
Reference:	MOLCAA 9558
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	24-2-2015
Revised date:	6-7-2015
Accepted date:	6-7-2015

Please cite this article as: M.Massaro, S.Riela, G.Cavallaro, C.G.Colletti, S.Milioto, R.Noto, F.Parisi, G.Lazzara, Palladium supported on Halloysitetriazolium salts as catalyst for ligand free Suzuki cross-coupling in water under microwave irradiation, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2015.07.008

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Palladium supported on Halloysite-triazolium salts as catalyst for ligand free Suzuki cross-coupling in water under microwave irradiation

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Graphical abstract

Highlights:

1. Triazolium materials were obtained by subsequent click reactions.

2. High loaded triazolium salt framework permitted the immobilization of Pd in high loading.

3. Catalyst was employed successfully in the Suzuki reaction in water under MW irradiation.

4. In this way Suzuki cross coupling meets the purposes of Green Chemistry

5. The catalyst showed good recyclability without any loss in activity and negligible Pd leaching.

ABSTRACT

Environmental friendly halloysite-dicationic triazolium salts (second generation) obtained by subsequent click reactions of a diyne derivative in the presence of 2-azidopropyl-modified halloysite nanotubes, were used as supports for palladium catalyst. Thanks to the high triazolium loading (25%) these materials were able to support higher amount of the metal

than that on the monocationic derivative (first generation). Such materials were characterized by thermogravimetric analysis, FT-IR spectroscopy and SEM investigations.

The new catalytic system was employed in the ligand free Suzuki cross-coupling under microwave irradiation. A set of solvent, time and % loading of palladium was screened. The palladium catalyst displayed good activity allowing the synthesis of several biphenyl in high yields working with only 0.1 mol% of palladium loading at 120 °C in water, for an irradiation time of 10 min. The second generation catalyst, also, showed good recyclability without any loss in activity and negligible palladium leaching that are significant improvements over the first generation triazolium catalyst.

Keywords: triazolium salt; multi-layered ionic liquids; halloysite nanotubes; Suzuki reaction; microwave

1. Introduction

Catalyst immobilization is a good opportunity to obtain materials that can be recovered and reused for several cycles with low leaching.

In this regard, palladium complexes or nanoparticles have been immobilized on various supports such as silica, alumina, zeolites, organic polymers, magnetic nanoparticles and dendrimers [1-8].

Several studies have been carried out on the use of ionic liquids as reaction media and as stabilizers for metal nanoparticles. In particular, great attention has been devoted to the use of supported ionic liquid phase (SILP)-based materials as heterogeneous recyclable palladium catalyst. In this context Gruttadauria et al. described a new kind of material constituted by a highly cross-linked imidazolium on the surface of silica gel. The multi-layered imidazolium salt frameworks permitted the immobilization of palladium in high loading (10 wt%) [9].

Moreover, it is known that when Pd is coordinated by a ligand, the bulkiness and electron-richness of the latter play important roles in achieving efficient catalytic activity with Pd. In the Suzuki–

Miyaura reaction indeed bulky ligands accelerate the reductive elimination step, while an electronrich ligand improves the insertion ability of Pd in the oxidative addition step, which is a key step in the catalytic cycle [10].

Recently, emerging materials with an appealing perspective for application in catalysis are halloysite nanotubes (HNTs) [11-13]. Halloysite is a natural, biocompatible, environmental friendly and cheap double-layered aluminosilicate mineral that has a predominantly hollow tubular structure. We have synthesized a palladium-based catalytic system using halloysite nanotubes modified with octylimidazolium moieties as support (HNT-SILLP/Pd) [14]. Imidazolium based ionic liquids are able to stabilize metal nanoparticles electronically and by coordination involving the cations, which protect against aggregation and/or agglomeration [15-17].

It was demonstrated that in some case supports based on triazole motif showed superior activity to the analogous imidazole molecules [18].

Triazolium salt can be synthesized in a straightforward, two-step procedure by copper(I)-catalyzed [3+2] cycloaddition of organic azides to alkynes in a click process [19], followed by N-alkylation. 1,2,3-Triazolium salts are much less acidic than imidazolium salts and, thus, can be inert under basic conditions where imidazolium-based ILs are deprotonated. Nevertheless, 1,2,3-triazolium salts were recently shown to undergo complex formation with palladium acetate by deprotonation at a ring carbon atom [20].

Ding et al., reported a new Pd catalyst for oxidation of benzyl alcohols based on silica-triazole support. The triazole moiety acts as a stable linker as well as a good chelator to participate in the catalytic reaction [21].

To the best of our knowledge there are no examples of the immobilization of palladium nanoparticles on heterogeneous ligand-free triazole support by electrostatic interactions.

Herein we report the synthesis of first and second generation of novel Pd-triazolium salts supports based on halloysite nanotubes (HNT-IL/Pd) (Figure 1); and we tested them in the Suzuki reaction under microwave irradiation using, in the best conditions, water as solvent. Indeed, in the last year

the use of water as reaction medium, for coupling reaction catalyzed by heterogeneous palladium catalyst has received considerable attention due to the rising concerns for the environmental since water is cheap, environmental friendly, and allows simple separation and catalyst recycling.

2. Experimental Section

2.1. General method

All reagents needed were used as purchased (Aldrich), without further purification. HNT-IL 1 and azido functionalized HNT was previous synthetized as reported in literature [22]. Halloysite was supplied by Applied Minerals. This material has an average tube diameter of 50 nm and inner lumen diameter of 15 nm. Typical specific surface area of this halloysite is 65 m²/g; pore volume of 1.25 mL/g; refractive index 1.54; and specific gravity 2.53 g/cm³.

Thermogravimetric analyses were performed by a Q5000 IR apparatus (TA Instruments) under a nitrogen flow of 25 cm³·min⁻¹ for the sample and 10 cm³·min⁻¹ for the balance. The weight of each sample was ca. 10 mg. The measurements were carried out by heating the sample from room temperature to 900 °C at a rate of 10 °C·min⁻¹. FTIR spectra were performed with a Beckmann DU 650 spectrometer. The microscope ESEM FEI QUANTA 200F was used to study the morphology of the functionalized HNTs. Before each experiment, the sample was coated with gold in argon by means of an Edwards Sputter Coater S150A to avoid charging under electron beam. MW-assisted synthesis were carried out with a CEM DISCOVER monomode system in closed vessel. ¹H-NMR spectra were recorded at 250 MHz in CDCl₃ solutions at room temperature on a Bruker AC-E Series 300 spectrometer.

2.2. Synthesis of 4,4' bis[2-(2-hydroxyethoxy)ethoxy]-diphenyl 1a

A solution of 4,4' byphenol (1 eq) in dry DMF (5.5 mL) was added to a stirred suspension of K_2CO_3 (3 eq) in dry DMF (15 mL) under argon. The mixture was stirred for 1 h at 60 °C. After this time, a

solution of 2-(2-chloroethoxy)-ethanol (2.6 eq) in dry DMF (8.1 mL) was added over 30 min, and the temperature was raised to 85 °C. Stirring and heating were continued for 7 days. After cooling to room temperature, the reaction mixture was filtered and the residue was washed with DMF (20 mL). The solvent was removed in vacuo and the residue was partitioned between CH_2Cl_2 and H_2O with addition of NaCl. The pH was adjusted to ca. 2 with 2 N HCl, and the organic phase was washed with H_2O , dried (MgSO₄), and concentrated in vacuo. The residue was purified by cromatography (Eluent: $CH_2Cl_2/MeOH 25:1$) and the product was obtained as red oil in yield of 30% (0.730 g).

¹H-NMR (300 MHz, CDCl₃) δ: 2.96 (s, 2H, OH); 3.46-3.55 (m, 12H, CH₂); 3.67-3.72 (m, 8H, CH₂); 4.06-4.10 (t, 4H, CH₂); 6.93-6.99 (m, 4H, CH); 7.23-7.32 (m, 4H, CH).

¹³C-NMR (300 MHz, CDCl₃) δ: 54.06; 62.37; 69.24; 70.36; 71.12; 71.49; 73.18; 113.13; 121.28; 129.09; 132.19; 157.01.

2.3. Synthesis of compound 1

Compound **1a** (500 mg, 1 eq) was dissolved in dry DMF (30 mL) and treated with NaH (1.12 g, 2.5 eq). After the evolution of gas ceased (~30 min), propargyl bromide (6 mL of 80% wt solution in PhMe, 6 eq) was added via a syringe. The mixture was left to stir at r. t. for 3 d. Solvent was removed in vacuo and the crude mixture was subjected to column chromatography (CH₂Cl₂ 100%, CH₂Cl₂/AcEt 1:1, AcEt 100% and AcEt/MeOH 10:1). 1 was obtained as brown oil in yield of 80%.

¹H-NMR (300 MHz, CDCl₃) δ: 1.59 (s, 2H, CH); 3.48-3.53 (m, 8H, CH₂); 3.59-3.71 (m, 12H, CH₂); 4.06-4.14 (m, 4H, CH₂); 4.15-4.19 (m, 4H, CH₂); 6.93-7.01 (m, 4H, CH); 7.25-7.31 (m, 4H, CH).

FTIR (nujol): 2114 cm⁻¹ stretching C=C; 2875 cm⁻¹ stretching CH₂; 3282 cm⁻¹ stretching =C-H.

2.4. Synthesis of compound 3

Azido functionalized halloysite 2 (500 mg) was suspended in a H₂O/t-BuOH 1:1 mixture (4 mL) and compound 1 (319 mg) was added. The mixture was stirred under argon in the presence of catalytic

amount of CuSO₄/sodium ascorbate solution (1 M, 1:10 v/v) at room temperature for 48 h. After this time, the solvent was filtered off, the powder was rinsed with H2O, then with NaOH 0.1 N and finally with CH_2Cl_2 . The powder was then dried at 80 °C under vacuum.

2.5. Synthesis of compound 4

Compound **3** (500 mg) was suspended in a H₂O/*t*-BuOH 1:1 mixture (4 mL) and NaN₃ (152 mg, 2.5 eq) was added. The mixture was stirred under argon in the presence of catalytic amount of CuSO₄/sodium ascorbate solution (1 M, 1:10 v/v) at room temperature for 48 h. After this time, the solvent was filtered off, the powder was rinsed with H₂O, then with NaOH 0.1 N and finally with CH₂Cl₂. The powder was then dried at 80 °C under vacuum.

Then it was suspended in dry toluene (100 mL) and an excess of the bromobutane was added. The suspension was then refluxed at 120 °C for 24 h. After this time, the solid was filtered off, rinsed with CH_2Cl_2 and finally dried at 80 °C under vacuum.

2.6. Typical Procedure for the Synthesis of the Palladium Catalysts 1 and 2

In a round-bottom flask were placed $PdCl_2$ (95 mg, 0.536 mmol), NaCl (626 mg, 10.72 mmol, 20 equiv.), HNT-IL **1** or **2** and toluene (13.6 mL). The flask was heated at 60 °C for 48 h, then filtered under reduced pressure, washed with Et_2O and water and dried overnight under reduced pressure at room temperature. The material was suspended in ethanol (10 mL) and to this suspension a solution of NaBH₄ (79 mg, 2.1 mmol, 7 equiv.) in ethanol (24 mL) was added dropwise. The suspension turned black and was stirred at room temperature for 6 h, then filtered under reduced pressure, washed with water and dried overnight under reduced pressure at room temperature.

2.7. Typical Procedure for the Suzuki Reaction via microwave irradiation

HNT-IL/Pd catalyst **1** or **2** (0.1 mol%), phenylboronic acid (65 mg, 0.547 mmol), K_2CO_3 (84 mg, 0.61 mmol), aryl bromide (0.55 mmol), ethanol (0.6 mL) and water (0.6 mL) or water (1.2 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 ¹H-NMR to calculate conversion.

2.8. Recyclability of the Catalyst

HNT-IL/Pd catalyst **1** or **2** (1mol%), phenylboronic acid (65 mg, 0.547mmol), K_2CO_3 (84mg, 0.615mmol), 3-bromoanisole (0.55mmol), ethanol (0.6ml) and water (0.6 ml) or water (1.2 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 reaction mixture was then centrifuged and the liquid mixture was decanted; the residual solid was washed with CH₂Cl₂, water and Et₂O. HNT-IL/Pd were dried and reused.

3. Results and Discussion

The first generation heterogeneous catalyst (HNT-IL/Pd **1**) was synthesized in two steps. First catalytic support was prepared by a synthetic route reported in literature [22]. The preparation of supported palladium nanoparticles, where the metal catalyst can be linked by electrostatic interactions in the HNT-IL support, was achieved by anion exchange from X^- to PdCl₄²⁻ (toluene solution of Na₂PdCl₄). The solid material, HNT-IL/(PdCl₄²⁻), was recovered by filtration and, finally, the Pd(II) was reduced to Pd⁰ with NaBH₄ in ethanol. Following this procedure, a HNT-IL catalyst with 5.3 wt% Pd was obtained as determined by energy-dispersive X-ray measurements (EDX). This loading was greater than the one obtained for HNT-imidazolium salt confirming the good ability, to act as stabilizer for palladium nanoparticles, showed by triazolium salts [21].

The catalyst was used in the Suzuki–Miyaura reaction between phenylboronic acid and a set of aryl halyde under experimental conditions previously adopted for imidazolium catalyst

[14]; i.e. in a mixture ethanol/water (1:1) at 120 °C in the presence of K_2CO_3 as base (Table 1). All the reactions were run for 10 min. The catalyst was used in 0.1 mol% loading. Conversions were high, ranging from 25% to 99%; in all case no byproducts were detected and the conversions reported in Table 1 correspond to yields. Full conversions were achieved when aryl bromides and iodides were employed (entries 1 and 7, respectively), while less reactive aryl chloride (entry 9) gave lower yield. Longer times of irradiation led to the degradation of compounds.

The next step was the recycling study of the catalytic material. Because of the very small amount of catalyst used (1 mg), we carried out recycling investigations using catalyst at 1 mol% in the reaction between phenylboronic acid and 3-bromoanisole (Table 2).

Catalyst was recovered by centrifugation and was reused in the same reaction in four cycles. Under the above conditions, catalyst afforded biphenyl-3-anisole in 94-85 % yield in three cycles, after that we observed a decrease in the yield. Atomic absorption spectroscopy (AAS) analysis of the washings after three cycles showed that 1.3% of palladium was released into solution during the course of a reaction. These results were different from that reported for HNT-imidazolium catalyst [14]; probably because the thermal stability of 1,2,3-triazolium salts (200-300 °C), is lower than that of 1,3dialkylimidazolium based ionic liquids (generally, $T_d>300$ °C) [23]. Therefore the triazolium could have a lower stability in the experimental conditions of Suzuki reaction under microwave irradiation. The loss of activity after three cycles could be ascribed to the thermal decomposition of triazolium salts on HNT surface and due to that we observed a greater Pd leaching.

To the light of these results, in order to improve the catalytic activity of HNT-IL, we designed a second generation HNT-triazole support (HNT-IL 2), based on dicationic triazolium salts. Dicationic ionic liquids, indeed, have high thermal stability, higher than that normally characterizing the corresponding monocationic; therefore, in terms of designing ionic liquids for specific applications, the dicationic ionic liquids open up the possibility to develop a new system with resistance to high

temperature [24]. Furthermore, for an application as support catalyst in the Suzuki reaction, the new support was designed with an aromatic linker to allow π - π interactions between catalyst and substrates and, therefore, facilitate the cross-coupling reaction. Such material, being high loaded (or multilayered) ionic liquid-like material, could be capable of stabilizing a higher amount of catalytically active Pd species [9]. Such an approach could furnish a catalytic material to be used in a low weight % compared to the substrates. This is certainly useful for large-scale applications.

The HNT-IL **2** was prepared as a result of four-step synthetic procedure as depicted in Figure 2. Compound **1** was synthetized following a procedure reported in literature (Figure 3) [25]. First alkylation of 4,4'byphenol with 2-(2-chloroethoxy) ethoxyethanol was carried out in DMF in the presence of K₂CO₃ as base. The product was purified by chromatography to yield the 4,4'bis[2-(2hydroxyethoxy)ethoxy]-diphenyl in yield of 30%. The subsequent propargylation was carried out by adding propargyl bromide in DMF and in the presence of NaH to give the product **1** in yields of 80%. Compound **1** reacts in the first step with azido-functionalized HNT **2**, prepared as reported previously [22], in a mixture *t*-BuOH/H₂O (1:1), in the presence of catalytic amount of CuSO₄ and sodium ascorbate for 48h at r.t. to give compound **3**. This material reacts in the second step with an excess of NaN₃ and finally, in the third step, by alkylation with butyl bromide, we have obtained the organic salt **4**.

The successful formation of the network of supported ionic liquids was confirmed by solid-state ¹³C NMR spectroscopy (Figure 4a). The characteristic signals of the carbon atoms of the triazolium ring are observed at $\delta = 168$ ppm, the signals of the aromatic moieties are observed in the range between 164 and 117 ppm, whereas the carbon atoms of ether groups resonate in the range 60–80 ppm. These data indicate that the main structure of the triazolium salts is not affected by the grafting process. The weak signals in the range 30-32 ppm are due to the aliphatic carbon atoms of triazolium salts. It is interesting to note that is not present the signal related to the silicon connected to the carbon atoms of the functionalized HNT (as confirmed from ²⁹Si NMR spectrum, Figure 4b). This result is not surprisingly, because the low loading of azido silane moiety onto HNT external surface (1.5%) [22].

The presence of the triazolium salts on the HNT was, also, confirmed by FT-IR spectra (Figure 5). Compared to azido HNT 2, compound 3 exhibited new bands around 1595 and 1348 cm⁻¹ due to C=C, N=N, C-N stretching vibrations of triazolium moiety. Furthermore, HNT-IL 2 did not show the stretching vibration band of C=C (2103 cm⁻¹) group, which was observed for compound 3. The FTIR spectrum of HNT-IL 2 was also characterized by the OH stretching vibrational bands of halloysite [14]. The frequencies of these bands were not altered in the functionalized nanotubes. Specifically, we observed the broad peak of the water OH stretch as well as the OH stretching vibration bands of the Al-OH and Si-OH groups. From these data, one can state that HNT-IL 2 were synthesized. These findings were confirmed by TG studies. In fact, the precursor of HNT-IL 2 (compound 4) exhibited the typical halloysite weight losses occurring at ca. 550 °C attributed to the expulsion of interlayer water molecules and the mass losses due to the thermal degradation of the organic moiety on HNT external surface (300-400 °C). After the alkylation, the degradation at 300-400 °C is absent and the organic moiety results stable up to 700 °C when a new degradation step is observed for HNT-IL 2 (Figure 6). Such a stabilization effect is expected for a dicationic salt. The catalyst support could benefit from increased thermal stability, which make it ideally suited for the often harsh conditions required in the Suzuki reaction. TG experiments allowed us to calculate the degree of HNT functionalization to be as ca. 25%. Although the rather high experimental error, EDX measurements confirmed the loading amount as from the N/Al weight ratio a loading of 36±20 % was calculated.

The surface morphology of HNT–IL 2 was investigated by SEM. As Figure 7 shows, the general feature of a tubular structure is preserved in the composite material but there is a change on the surface properties. In particular, a smooth surface is observed in comparison to pristine HNT [26]. This peculiarity can be explained by considering the high loading of organic moiety on HNT outer surface and the strong π - π interactions between aromatic rings.

Loading of palladium was performed as previously described for first generation catalyst. A HNT-IL **2** catalyst with 6.3 wt% Pd was obtained as determined by EDX measurements. The introduction of two triazole rings and a linker between them, onto the support could change system's properties, so in order to optimize reaction conditions such as reaction temperature, time and amount of palladium catalyst, we performed several test reactions. To find the best conditions, the reaction between 3-bromoanisole and phenylboronic acid was chosen as model reaction, for which influences of different parameters were examined to obtain the best possible combination. The parameters included solvent, reaction time and catalyst concentration. Since it is known that an important parameter is represented by the reaction medium, the first step was a solvent study. Six reaction media were examined, namely EtOH/H₂O 1:1, ethanol, toluene, acetonitrile, 1,4 dioxane and water (Table 3). Organic solvents (entries 1-4) gave low yield for the reaction.

However, when we adopted the organic/aqueous co-solvent, an increasing in the yield was observed (entry 5). Surprisingly, high yield was obtained when we used as solvent pure water. Next the effect of reaction times on the Suzuki reaction in H₂O, were examined. The best experimental conditions were obtained with an irradiation time of 10 min; indeed, with longer times, conversions decreased (Table 3, entry 8). To estimate the effects of the amount of Pd catalyst on the conversion reaction, we performed an additional reaction with 0.1 mol% catalyst, resulting in quantitative conversion (entry 9). HNT-IL/Pd **2** was used in the Suzuki–Miyaura reaction between phenylboronic acid and a set of aryl halide in water at 120 °C in the presence of K_2CO_3 as base. All the reactions were run for 10 min. HNT-IL/Pd **2** was used in 0.1 mol% loading. The results were summarized in Table 4. Conversions were high with yields up to 99% in the case of anisole derivatives, on the contrary, other substrates gave lower yields in water but we observed an increasing in conversion in a mixture water/ethanol (1:1),

The merit of the co-solvent may be attributed to the good solubility of the organic reactants and the inorganic base. In this case, yields were similar to those obtained with HNT-IL **1**.

The excellent conversions obtained for anisole derivatives could be due to a synergic effect of ethereal alkyl chains or aromatic rings, present in the catalyst support and microwave irradiation on cross-coupling of anisole in water. This indicates that the electron-richness of the support promoted the ability for oxidative addition [10a], which is a crucial step in enhancing the catalytic activity of catalyst in the Suzuki coupling reaction. The next step was the recycling study of the catalytic materials **2**. Also in this case, recycling investigations were carried out using catalyst **2** at 1 mol% in the reaction between phenylboronic acid and 3-bromoanisole (Table 5). Catalyst was recovered by centrifugation and was reused in the same reaction in five cycles. Under the above conditions, catalyst **2** afforded biphenyl-3-anisole in 99-90 % in five cycles.

In order to determine the degree of leaching of the metal from heterogeneous catalyst, the catalyst was recovered by centrifugation after the reaction was completed and the palladium content of the supernatant was determined by AAS. It was shown that less than 0.01% of the total amount of the original palladium species was lost into solution during the course of a reaction, therefore the leaching level was negligible, which was also confirmed by the excellent recoverability and reusability of this heterogeneous catalyst. The low leaching in Pd catalysts immobilized on to gel-supported ionic-liquid phase has been ascribed to a 'release and catch' mechanism [27]. 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 [27c]. It is worth noting that the enhanced catalytic performance of HNT-IL/Pd **2** can be also due to the thermal stability of this support. This hypothesis was confirmed by FT-IR spectroscopy. The spectrum of the catalyst was not altered by the catalytic process (see Figure 8).

4. Conclusions

In summary, first and second generation of environmental friendly halloysite-triazolium salt catalysts were prepared. The dicationic triazolium materials were obtained by subsequent click reactions of a dyine derivate in the presence of 3-azidopropyl-modified halloysite. This synthetic procedure allowed the realization of high loaded triazolium salt framework (25%) which permitted the immobilization of palladium in high loading after exchange of halogen ions with tetrachloropalladate ions, in toluene, and reduction with sodium borohydride. Materials were characterized by several techniques. In particular from TGA results, it was demonstrated that the dicationic catalyst support had good thermal stability therefore it is suited for the harsh condition required in the Suzuki reaction under microwave irradiation.

The first generation catalyst was not stable in these experimental conditions as highlighted from recyclability tests.

The second generation catalyst was employed successfully in the Suzuki cross coupling for the synthesis of several biaryl working only with water as solvent.

Thanks to the high palladium loading, only 1 mg of catalyst per mmol of substrate was employed. In addition the reaction works in the absence of organic co-solvent. All these aspects ensures Suzuki cross coupling meets the purposes of Green Chemistry.

Recycling of catalyst was, also, investigated. These experiments with 3-bromoanisole in water gave the corresponding biaryl in excellent yields after five cycles. Therefore this material showed good recyclability without any loss in activity and negligible palladium leaching, facts that are significant improvements over the first generation triazolium catalyst.

Acknowledgements

The work was financially supported by the University of Palermo, PRIN 2010-2011 (prot. 2010329WPF) and FIRB 2012 (prot. RBFR12ETL5). The authors would thanks Prof. S. Orecchio (University of Palermo) for AAS measurements. 1H-NMR spectra were provided by Centro Grandi

Apparecchiature-UniNetLab – Università di Palermo funded by P.O.R. Sicilia 2000–2006, Misura 3.15 Quota Regionale.

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Figure Captions:

Figure 1. Schematic representation of catalytic supports a) first generation; b) second generation, synthesized.

Figure 2. Schematic representation of the synthesis of HNT-IL 2 support.

Figure 3. Synthesis of compound 1.

Figure 4. Solid-state (a) ¹³C NMR and (b) ²⁹Si NMR spectra of HNT-IL 2.

Figure 5. FT-IR spectra of (a) compound 2; (b) compound 3 and (c) HNT-IL 2.

Figure 6. Derivative thermogravimetric curves of compound 4 and HNT-IL 2.

Figure 7. SEM images of HNT-IL 2.

Figure 8. FT-IR spectra of HNT-IL 2 (a) before and (b) after catalysis.

 Table 1. Suzuki–Miyaura reactions between phenylboronic acid and aryl halides catalyzed by HNT-IL 1.

 \wedge

BO	$ \begin{array}{c} \mathbf{b}_2 \\ \mathbf{b}_2 \\ \mathbf{b}_2 \\ \mathbf{b}_2 \\ \mathbf{b}_2 \\ \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}$	OCH3
Entry	Ar-X	Conversion (%) ^{a)}
1	4-bromoacetophenone	>99
2	3-bromoacetophenone	65
3	4-bromobenzaldheyde	>99
4	4-bromoanisole	83
5	3-bromanisole	95
6	4-bromoaniline	58
7	4-iodoacetophenone	>99
8	4-iodoanisole	>99

9 4-chlorobenzaldheyde 25

^{a)} Determined by ¹H-NMR.

 Table 2. Recycling investigation.

Entry	Cycle	Conversion (%) ^{a)}
1	1	95
2	2	86
3	3	85
4	4	27

^{a)} Determined by ¹H-NMR.

 Table 3. Optimization of experimental conditions for Suzuki cross-coupling reaction under microwave irradiation.



Entry	Solvent	Time	Pd	Conversion
	((mol%)	(%) ^{a)}
Solvent effect				
1	Acetonitrile	10	1	18

2	1,4 Dioxane	10	1	20
3	EtOH	10	1	25
4	Toluene	10	1	43
5	H ₂ O/EtOH (1:1)	10	1	78
6	H ₂ O	10	1	96
Time effect				
7	H ₂ O	5	1	89
8	H ₂ O	15	1	80
Pd loading				
9	H ₂ O	10	0.1	>99

^{a)} Determined by ¹H-NMR.

Table 4. Suzuki cross-coupling reaction of ohenylboronic acid with various aryl halides under optimized reaction

 conditions under microwave irradiation.



2	4-bromoanisole	>99	
3	3-bromoacetophenone	25	65
4	4-bromoacetophenone	49	
5	3-bromobenzaldheyde	39	
6	4-bromobenzaldehyde	58	85
7	4-bromoanisole	>99	
8	1-bromo-4-nitrobenzene	25	
9	1-bromo-2,4,6- triisopropylbenzene	<5	
10	3-iodoanisole	>99	
11	4-iodoanisole	>99	
12	4-chlorobenzaldehyde	<5	

^{a)} Determined by ¹H-NMR.

 Table 5. Recycling investigation.

Entry	Cycle	Conversion (%) ^{a)}
1	1	>99

2	2	>99
3	3	>99
4	4	90
5	5	90

^{a)} Determined by ¹H-NMR.