



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



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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.

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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 electron-rich 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-SILP/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].

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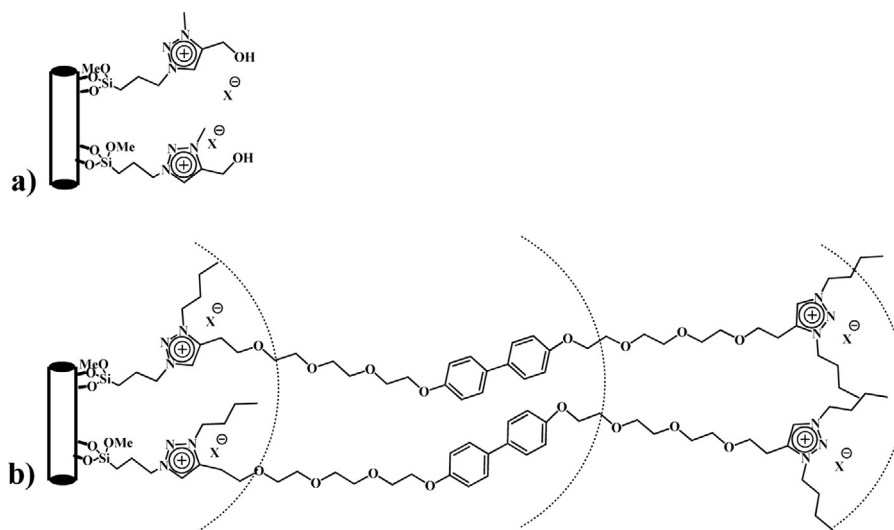


Fig. 1. Schematic representation of catalytic supports a) first generation; b) second generation, synthesized.

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) (Fig. 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 environment 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 previously synthesized 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 Avance II 400 MHz spectrometer. Solid state ¹³C and ²⁹Si NMR spectra were obtained at room temperature through a Bruker Avance II 400 MHz (9.4 T) 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 K₂CO₃ (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 CH₂Cl₂ and H₂O with addition of NaCl. The pH was adjusted to ca. 2 with 2 N HCl, and the organic phase was washed with H₂O, dried (MgSO₄), and concentrated in vacuo. The residue was purified by chromatography (Eluent: CH₂Cl₂/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%.

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