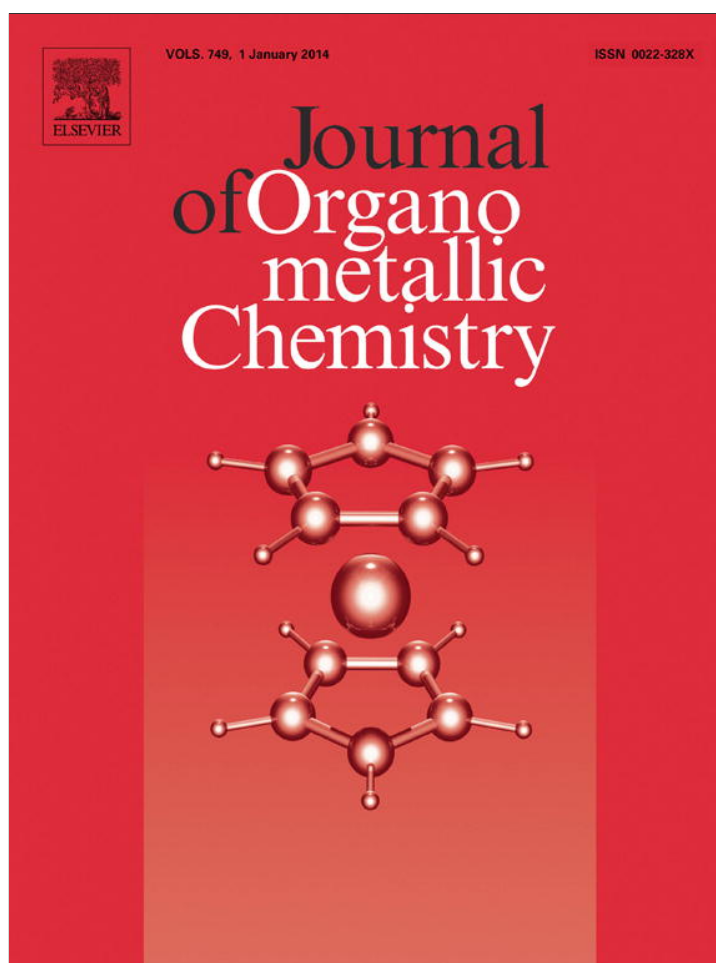


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Eco-friendly functionalization of natural halloysite clay nanotube with ionic liquids by microwave irradiation for Suzuki coupling reaction

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ABSTRACT

Microwave assisted halloysite (HNT) external surface functionalization with ionic liquids is described. HNTs modification was achieved in two steps: a) grafting of 3-mercaptopropyl trimethoxysilane on the external surface of HNT by a microwave irradiation; b) anchorage of vinylimidazolium ionic liquids by a thiol-ene reaction. MW irradiation allowed us to obtain high loading onto the HNT surface compared to those obtained through conventional synthesis. Fourier transform infrared spectroscopy and thermogravimetric analysis confirmed that the grafting has occurred only on the external surface of HNT. Turbidimetric and dynamic light scattering analyses showed that the introduction of ionic liquid on the HNT surface involves the formation of aggregates. One of these materials has been used as support for Palladium particles and tested, as catalyst, in the Suzuki reaction between phenylboronic acid and some aryl halide to give the corresponding biaryl in high yield. A catalytic efficiency higher than conventionally used support was achieved.

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Halloysite nanotube (HNT) is an emerging biocompatible material with appealing perspective for technological applications, such as in catalysis [1] and in pharmaceutical research [2].

Furthermore, HNT was used as green filler for the preparation of polymer composites with improved mechanical [3] and thermal properties [4]. Moreover, smart nanocomposites with self-healing functions [5] were obtained by doping a polymer matrix with HNT functionalized by biologically active molecules.

Halloysite is a naturally occurring mineral nanoclay with a tubular shape and a stoichiometry of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ which is different to kaolinite only for the presence of two molecules of water located between the adjacent clay layers [6]. As concerns the size, HNTs are quite polydisperse with a length ranging between 0.1 and 2 μm while the outer and inner diameters are ca. 30–50 nm and 1–30 nm, respectively [7]. The internal surface consists of gibbsite octahedral sheet (Al–OH) groups whereas the external surface is composed of siloxane groups (Si–O–Si) [8]. Due to the different chemistry properties of outer and inner walls these nanoparticles have a negatively charged outer surface and a

positively charged inner lumen, in water, in the pH range 2–8 [9]. The negative charge on the outer surface was used in the production of halloysite multilayer films by layer-by-layer nanoassembly [10]. The functionalization of the lumen with anionic macromolecules, such as biocides, pharmaceuticals, enzymes and other chemically active agents, is an efficient strategy to obtain smart nanomaterials attractive for anticorrosion protective coating, drug immobilization and controlled release, water purification [7,11,12]. Inorganic micelles with high affinity towards hydrophobic compounds were successfully prepared by selective modification of HNT lumen [2a,13]. The functionalization of HNTs is a good strategy to introduce an organic moiety onto the external surface and, therefore, to obtain innovative catalyst supports as demonstrated for the metalloporphyrin [14] immobilization and the heterogeneous Atom Transfer Polymerization of methyl methacrylate (MMA) into poly(methyl methacrylate) (PMMA) by using CuBr as catalyst [15]. HNTs were used as catalyst support for the platinum in the synthesis of allyl-ended hyperbranched organic silicone resins [16]. The non-covalent functionalization of HNTs external surface, with ionic liquids (ILs) was, also, reported. The interaction between 1-butyl-3-methyl-imidazolium hexafluorophosphate [BMIm]PF₆ and HNTs, proposed by hydrogen bonds, was verified by various spectral results and the IL-coated-HNTs were used as reinforcement for styrene-butadiene rubber [17].

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No examples are reported in the literature about the covalent functionalization of HNTs external surface with ILs. In recent years SILLP (supported ionic liquid-like phase)-based materials prepared by covalent attachment have been synthesized [18,19]. The preference for heterogeneous catalytic systems based on SILLP compared to the corresponding homogeneous ionic liquid phase is motivated by the advantage of easy separation and the ability to use fixed-bed reactors. These materials can be used for many purposes, such as catalysts or support for catalytic species, and toward this goal, our group has devoted many efforts. A recent application has been the obtainment of an easily recoverable palladium catalyst for Suzuki coupling reaction. The materials that we have employed, as supports, were amorphous silica gel or mesoporous silica SBA-15 [18].

In this work we describe a new synthetic method for HNTs modification, which consists in the following steps: a) grafting of 3-mercaptopropyl trimethoxysilane on the external surface of HNT by a microwave irradiation and b) anchorage of vinylimidazolium ionic liquids by a thiol-ene reaction (Fig. 1). One of these materials has been used as support for Palladium particles and tested, as catalyst, in the Suzuki reaction.

1. Experimental section

1.1. Materials

All reagents needed were used as purchased (Aldrich), without further purification.

Ionic liquids were synthesized as previous reported [20].

1.2. Synthesis of thiol functionalized halloysite nanotubes (f-HNT)

1.2.1. Classical procedure [21]

Organosilane modified samples were prepared according to the procedure generally applied for the grafting of silica-based materials. In a typical run, 1 mL of 3-mercapto-propyl trimethoxysilane was dissolved in 20 mL of dry toluene. Approximately 3 g of clay powder was added, and the suspension was dispersed ultrasonically for 20 min.

The suspension was then refluxed at 120 °C for 20 h under constant stirring.

The solid phase in the resultant mixture was filtered and extensively washed with MeOH to remove the excess organosilane, then dried overnight at 80 °C under vacuum.

1.2.2. Microwave irradiation

First, 1 g of HNT was suspended in a MW test tube provided with a cap, in 5 mL of dry toluene and then 2 mL of 3-mercaptopropyl trimethoxysilane was added dropwise. The suspension was dispersed ultrasonically for 5 min at room temperature and inserted in MW apparatus at 80 °C and a power of 10 W, under constant

stirring for 1 h. The powder was filtered, rinsed with MeOH and dried at 80 °C under vacuum.

1.2.3. Solvent-free MW irradiation

First, 1 g of HNT was weighted in a MW test tube provided with a cap, and 2 mL of 3-mercaptopropyl trimethoxysilane was added dropwise. The mixture was dispersed ultrasonically for 5 min at room temperature and inserted in MW apparatus at varying temperatures (80, 100, 140 and 180 °C) and a power of 25 W, under constant stirring for 0.5, 1, 3 h. The powder was filtered, rinsed with MeOH and dried at 80 °C under vacuum.

1.3. General synthesis for the ionic liquid modified halloysite nanotubes (f-HNT-IL)

1.3.1. Classical procedure [22]

Thiol functionalized HNTs (0.500 g) was suspended in dichloromethane (7.5 mL) and the appropriate ionic liquid (2.0 mmol) was added. The mixture was stirred, under argon, in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) at reflux temperature for 42 h. After cooling, the solvent was filtered off and the powder was rinsed with CH₂Cl₂ to remove excess of ionic liquid and then dried at 80 °C under vacuum.

1.3.2. Microwave irradiation

Thiol functionalized HNTs (0.100 g) was suspended in dichloromethane (2 mL) and the appropriate ionic liquid (0.4 mmol) was added. The mixture was dispersed ultrasonically for 5 min at room temperature and inserted in MW apparatus at 40 °C and a power of 1 W, under stirring for 1 h. The powder was filtered, rinsed with CH₂Cl₂ and dried at 80 °C under vacuum.

1.3.3. Solvent-free MW irradiation

Thiol functionalized HNTs (0.100 g) was weighted in a MW test tube provided with a cap and the appropriate ionic liquid (0.4 mmol) was added. The mixture was dispersed ultrasonically for 5 min at room temperature and inserted in MW apparatus at 50 °C and a power of 1 W, under stirring for 1 h. The powder was filtered, rinsed with CH₂Cl₂ and dried at 80 °C under vacuum.

1.4. Typical procedure for the synthesis of the palladium catalysts HNT-Pd [18]

In a round-bottom flask were placed PdCl₂ (5.5 mg, 0.031 mmol), NaCl (36 mg, 0.062 mmol, 20 equiv.) and water (1 mL). The flask was heated at 80 °C until the PdCl₂ was dissolved. This clear reddish solution was cooled at room temperature and added to a suspension of f-HNT-IL (475 mg) in water (4 mL). The suspension was stirred at room temperature for 20 h, then filtered under reduced pressure, washed with water and dried overnight under reduced pressure at room temperature. The material was suspended in ethanol (12 mL)

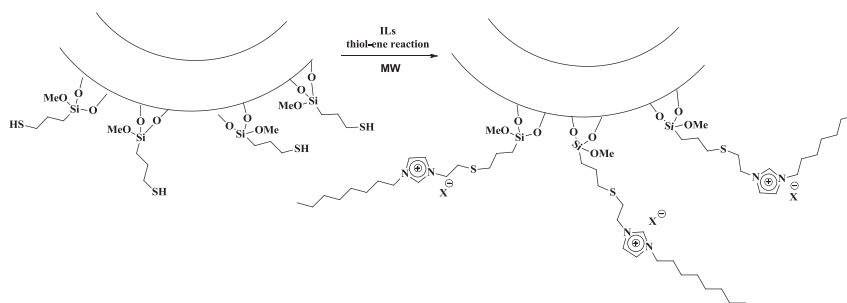


Fig. 1. Schematic illustration of ILs anchorage onto HNTs external surface.

and to this suspension a solution of NaBH_4 (8 mg, 0.217 mmol, 7 equiv.) in ethanol (12 mL) was added dropwise. The suspension turned black and it 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.

1.5. Typical procedure for the Suzuki reaction

In a round-bottom flask catalyst HNT-Pd (1 mol%), phenylboronic acid (65 mg, 0.533 mmol), K_2CO_3 (85 mg, 0.606 mmol, 1.14 equiv.), 4-bromo acetophenone (0.567 mmol), ethanol (0.6 mL) and water (0.6 mL) were placed. The reaction mixture was stirred at 50 °C.

After 19 h, the solvent was removed under reduced pressure and the residue was checked by ^1H NMR to calculate the conversion.

1.6. Recyclability of the catalyst

Catalyst HNT-Pd (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 an MW test tube provided with a cap. The mixture was inserted in MW apparatus at the temperature of 120 °C and a power of 14 W, under constant stirring for 10 min. Then, the reaction mixture was centrifuged and the liquid mixture was decanted, the residual solid was washed with CH_2Cl_2 , water and Et_2O . HNT-Pd was dried and reused.

1.7. Instrumentation

MW-assisted syntheses were carried out with a CEM DISCOVER monomode system in closed vessel.

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.

The experiments were performed by means of a Q5000 IR apparatus (TA Instruments) under the nitrogen flow of $25\text{ cm}^3\text{ min}^{-1}$ for the sample and $10\text{ cm}^3\text{ min}^{-1}$ for the balance at the heating rate of 10 °C min^{-1} . Temperature spanned from ambient to 900 °C.

FT-IR spectra in KBr pellets were determined at room temperature in the spectral region $400\text{--}4000\text{ cm}^{-1}$ using a Frontier FT-IR spectrometer (Perkin–Elmer). The spectral resolution is 2 cm^{-1} .

The measurements were performed at $22.0 \pm 0.1\text{ °C}$ in a sealed cylindrical scattering cell at a scattering angle of 90° by means of a Brookhaven Instrument apparatus composed of a BI-9000AT correlator and a He–Ne laser (75 mW) with a wavelength (λ) of 632.8 nm. The solvent was filtered by means of a Millipore filter with $0.45\text{ }\mu\text{m}$ pore size. For all systems, the field-time autocorrelation functions were well described by a mono-exponential decay function, which provides the decay rate (I) of the single diffusive mode. For the translational motion, the collective diffusion coefficient at a given concentration is $Dt = I/q^2$ where q is the scattering vector given by $4\pi n\lambda^{-1}\sin(\theta/2)$ being n the water refractive index and θ the scattering angle.

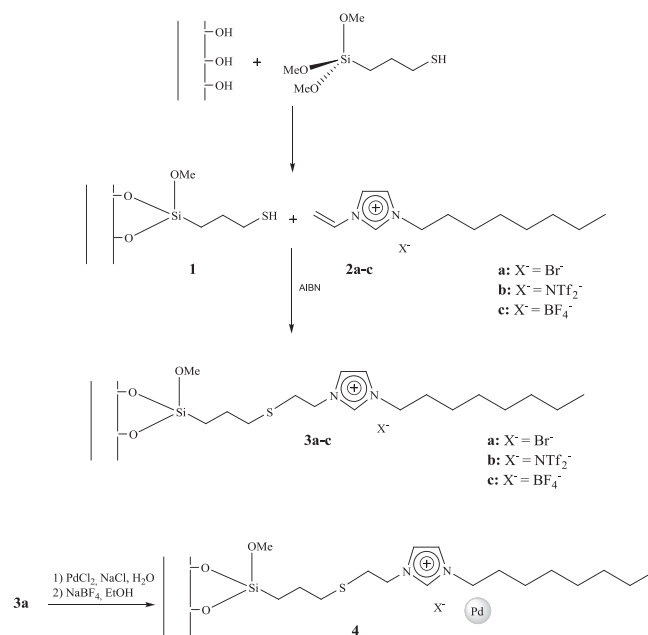
Turbidimetric measurements were performed with a Beckmann DU 650 spectrometer.

NMR spectra were recorded on a Bruker AC-E Series 300 spectrometer.

2. Results and discussion

2.1. Synthesis and properties of functionalized nanotubes

The synthesis of the catalytic material HNT-Pd was accomplished in three steps, as depicted in Scheme 1 while the suitable



Scheme 1. Synthesis of HNT based supported ionic liquid phase materials and catalyst HNT-Pd.

experimental conditions are reported in Tables 1 and 2. In the first step, the reaction between the hallosite nanotubes and an excess of 3-mercaptopropyl trimethoxysilane gave the f-HNT material **1**; in the second step, **1** reacts with an excess of 1-vinyl 3-octyl imidazolium salt **2**, in the presence of azobisisobutyronitrile (AIBN) to give f-HNT-IL materials **3**; finally, in the third step, the f-HNT-IL **3a** obtained was used as support for the immobilization of Palladium catalyst (material **4**).

In Table 1 are shown the experimental conditions used to synthesize the material **1** by the functionalization of HNT external surface. We investigated the synthetic procedure reported in literature [21] (entry 1) and afterward we repeated the experiments by microwave irradiation in the same solvent (entry 2).

It is noteworthy that after 1 h of MW irradiation (entry 2) we have observed an approximately double increase in loading rate of organosilane onto the HNT surface compared to traditional synthesis (entry 1), which takes 20 h (Table 1).

Since toluene solvent shows low ability to convert electromagnetic energy into heat ($\tan \delta = \epsilon''/\epsilon' = 0.040$; ϵ' = dielectric constant, ϵ'' = dielectric loss), in order to developing eco-friendly synthetic way we used the solvent-free conditions in other experiments (entries 3–8).

The best experimental conditions, in which the loading was 2.1%, are shown in entry 4 when we used an irradiation time of 1 h

Table 1
Experimental conditions and organosilane loading obtained for Step 1.

Entry	Heating	Solvent	Time (h)	Temperature (°C)	Loading (wt%) ^a
1	Trad. ^b	Toluene	20	120	0.8
2	MW	Toluene	1	80	2.2
3	MW	Free	1	80	0.7
4	MW	Free	1	100	2.1
5	MW	Free	0.5	100	1.3
6	MW	Free	3	100	1.3
7	MW	Free	1	140	1.3
8	MW	Free	1	180	1.5

^a From TGA results.

^b Traditional heating: HNT (3 g), 3-mercaptopropyl trimethoxysilane (5.4 mmol), toluene (20 mL), 20 h, reflux.

Table 2
Experimental conditions and IL loading for Step 2.^a

Entry	Heating	Solvent	X ⁻	Time (h)	T (°C)	Loading (wt%) ^b
1	Trad. ^c	DCM	NTf ₂ ⁻	42	50	0.4
2	MW	DCM	NTf ₂ ⁻	1	40	1.8
3	MW	Free	NTf ₂ ⁻	1	50	2.1
4	MW	Free	Br ⁻	1	50	4.9
5	MW	Free	BF ₄ ⁻	1	50	0.5

^a IL = 1-vinyl 3-octyl imidazolium bis (trifluoromethylsulfonyl)amide.

^b From TGA results.

^c Traditional heating: HNT (0.5 g), ionic liquid (2.0 mmol), AIBN (cat.), CH₂Cl₂ (7.5 mL), 42 h, reflux.

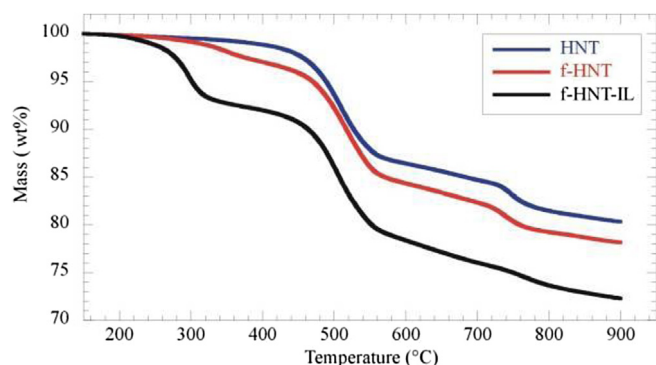


Fig. 2. TG curves for pristine HNT, f-HNT (entry 4, Table 1) and f-HNT-IL (entry 4, Table 2).

and a temperature of 100 °C. Reaction time less than 1 h (entry 5) gave compound **1** in which the loading was 1.3%, such as irradiation time of 3 h (entry 6). This result could be explained as follows: in the first case the reaction did not go to completion; while in the second case, longer times of irradiation lead to degradation of

compounds. The latter process was observed when the temperature was increased from 100 to 180 °C (entries 7, 8).

Microwaves and solvent-free conditions improved, in all cases, the grafting of the organosilane onto the hydroxyl groups from the external surface. In general, we have obtained a higher loading with respect to that previously reported in literature (lower than 1%) [23].

In all experiment, the loading (wt%) was estimated by thermogravimetric analysis. Thermogravimetry is an appropriate technique to evaluate the loading of organic molecules grafted onto nanoparticles surfaces [4]. Some examples of the mass loss curves are reported in Fig. 2.

The mass loss occurring from 200 to 400 °C is attributed to the degradation of organosilane groups grafted onto the nanoclay. Given that the mass loss of pristine HNTs is almost negligible in this temperature range, the loading was successfully calculated from the TG curves.

It is interesting to note the different degree of loading of HNT when compared with silica modified support; in fact the loading of organosilane on silica gel surface was 1.2 mmol g⁻¹ [18], while only 0.15 mmol g⁻¹ was loaded on HNT surface. Although the functionalization involves Si–OH groups, in both support, the different behavior could be attributed to a greater surface area of silica compared to that of HNT.

In Table 2 are shown the experimental conditions used for the covalent linkage of 1-vinyl 3-octyl imidazolium salt to f-HNT.

Several routes were checked, such as the conventional reaction reported for silica gel (entry 1) [21], and the heating by microwave irradiation (entry 2). As above mentioned, since DCM has the same behavior of toluene ($\tan \delta = 0.042$) we have employed solvent-free conditions, too (entries 3–5).

To evaluate the effectiveness of each route for step 2 in the synthesis (Scheme 1), we focused on the IL content that was estimated from TG data by comparing the mass loss from 200 to 400 °C for f-HNT and the corresponding f-HNT-IL.

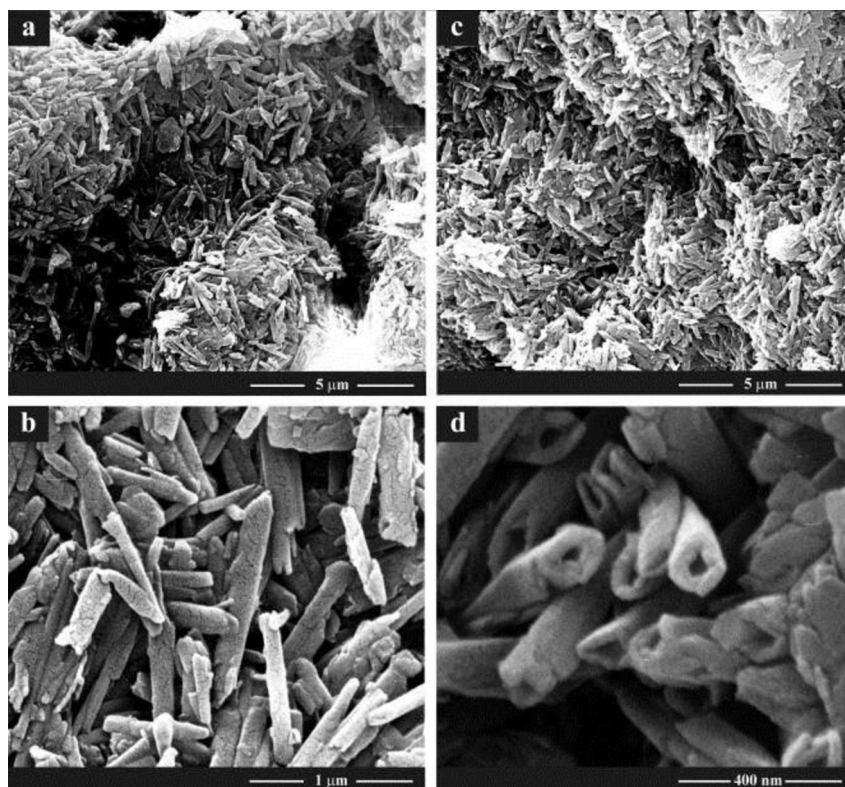


Fig. 3. Scanning electron microscopy images of: a, b, f-HNT (entry 4, Table 1); c, d, f-HNT-IL (entry 3, Table 2).

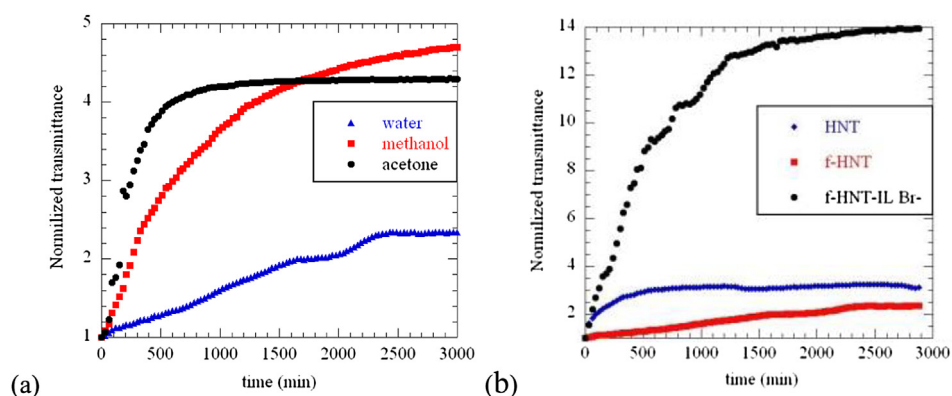


Fig. 4. Optical transmittance normalized for the initial value as a function of time for (a) f-HNT dispersions in various solvent; (b) HNT, f-HNT and f-HNT-IL dispersions in water. The concentration is 0.1 wt% in all cases.

One may note that the solvent-free and MW irradiation is the most efficient procedure to bind ionic liquid on the f-HNT (Table 2). Moreover, the IL loading decreases with the anion counterion size (Table 2). FTIR investigation on both f-HNT and f-HNT-IL shows that the vibrational bands of HNTs remain unaltered after the reactions (data are in Supplementary information). The frequency and assignments of each vibrational mode are based on previous reports on halloysite [21,24–28]. Compared to pristine HNT, f-HNT exhibits the vibration bands for C–H stretching of methylene groups around 2930 cm^{-1} , stretching of terminal methyl groups at 2850 cm^{-1} , the deformation of CH_2 at 1470 cm^{-1} . In the f-HNT-IL material, the stretching of $\text{CH}=\text{CH}$ and $\text{C}=\text{N}$ aromatic groups around 3000 and 1600 cm^{-1} are also observed. These findings evidence the presence of the silane moieties in f-HNT and, based on the unaltered frequency of stretching bands of the OH of the inner-surface Al–OH groups, we can conclude that grafting has taken place only on the external surface of HNT. The TG data corroborate this hypothesis. The ratios between the mass loss at ca. $450\text{ }^\circ\text{C}$, related to the two water molecules from the HNT crystal structure calculated, and the one due to the dehydroxylation of alumina at ca. $700\text{ }^\circ\text{C}$ for all f-HNT and f-HNT-IL samples are roughly similar to that calculated from the clay unitary cell formula.

Direct observation of the surface morphology of f-HNT and f-HNT-IL was carried out by scanning electron microscopy (SEM). As Fig. 3 shows, the tubular shape of the nanoclay is not lost upon the grafting of the organosilane and the binding of the IL. Moreover, the



Fig. 5. Scanning electron microscopy images of HNT-Pd.

lumen of the nanotube is empty after functionalization in agreement with the previously reported data. Comparing the SEM images of f-HNT and f-HNT-IL with the one from pristine [4a] it turned out that the average characteristic sizes of the nanoparticle are not altered.

2.2. Colloidal stability of functionalized nanotubes

Turbidimetric analyses were performed to highlight the influence of functionalization on the dispersion stability of HNT in solvent media, which might be crucial for application as catalyst in heterogeneous phase.

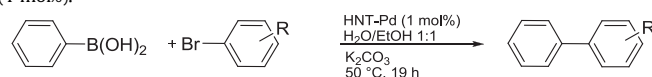
f-HNT dispersion showed a higher stability in water than in methanol and acetone (Fig. 4a). The introduction of ionic liquid decreases the stability in water as a consequence of a more hydrophobic external surface of the nanotubes (Fig. 4). The stability of dispersion of f-HNT-IL Br^- in water was the worst observed among the investigated samples, but it is better than the stability of dispersions of HNT-IL BF_4^- and HNT-IL NTf_2^- .

Dynamic Light Scattering (DLS) experiments allowed us to investigate the diffusion behavior of functionalized HNT. The average translational diffusion coefficients (D_t) in water of f-HNT ($1 \times 10^{-12}\text{ m}^2\text{ sec}^{-1}$) and f-HNT-IL ($3 \times 10^{-13}\text{ m}^2\text{ sec}^{-1}$) are both almost independent on concentration (see Figure in SI).

The f-HNT synthesized by MW and MW solvent-free procedures present D_t values very close to those reported for bare HNTs in water ($9.4 \times 10^{-13}\text{ m}^2\text{ sec}^{-1}$) indicating that they possess the same diffusion dynamic behavior of single diffusive nanotubes. The introduction of IL with Br^- anion determines a decrease of D_t which is due to the presence of hydrophobic attractive interactions generated by the chains of the IL located at the outer HNT surface. Therefore, the low stability of f-HNT-IL- Br^- aqueous dispersion, observed by turbidimetry, can be explained on the basis of its tendency to form aggregates. The even lower stability for the f-

Table 3

Suzuki reaction between phenylboronic acid and aryl bromide catalyzed by HNT-Pd (1 mol%).

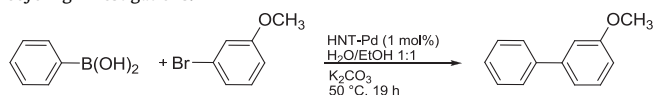


Entry	R	Conversion ^a (%)	Yield ^a (%)	Conversion ^b (%)	Yield ^b (%)
1	4-CHO	66	66	81	81
2	4-COCH ₃	92	92	88	88
3	3-OCH ₃	92	92	85	85

^a HNT-Pd catalyst.

^b SiO_2 -Pd catalyst.

Table 4
Recycling investigations.



Entry	Cycle	Conversion (%)	Yield (%)
1	1	92	92
2	2	90	90
3	3	88	88
4	4	88	88

HNT-IL with BF_4^- and NTf_2^- aqueous dispersions did not allow us to perform reliable DLS experiments.

2.3. Catalytic activity of functionalized nanotubes

The preparation of supported palladium HNT nanoparticles was carried out by anion exchange, from Br^- to PdCl_4^{2-} in water. Afterward, the Pd(II) was reduced to Pd^0 with NaBH_4 in ethanol [18]. Following this procedure, a Palladium catalyst with 0.7 wt% of Pd is obtained as determined by EDX measurements. This value is in agreement with the theoretical value of 1.1 wt% calculated on the basis of the stoichiometry. The SEM images of the obtained catalyst show that the tubular hollow shape is still preserved after the last step of the synthesis (Fig. 5).

We have tested the catalytic activity of HNT-Pd support in the Suzuki reaction between phenylboronic acid and some aryl bromide (Table 3) in ethanol/water at 50 °C in the presence of K_2CO_3 as base for 19 h. Catalyst HNT-Pd 4 was used in a 1 mol% loading.

Conversions were high with yields ranging from 66 to 92%.

The catalyst 4 was reused for several cycles (Table 4). 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 catalyst could be reused for four runs keeping the high reactivity and selectivity.

Recently Diebold et al. reported the synthesis of heterogeneous palladium catalyst supported on a rasta resin for Suzuki cross-coupling; they afforded the desired biaryl derivative in yield less than the one obtained by us, in the presence of 1 mol% of supported Pd, too [29]. In addition is remarkable to note that the HNT-Pd catalyst 4 appears to be more efficient than those we used previously on silica support (Table 3) [18].

3. Conclusions

Modification of external surface halloysite nanotubes with ionic liquids by microwave irradiation was demonstrated.

In particular we have obtained higher loadings in solvent-free conditions; making the reaction green.

Successful functionalization was demonstrated with IR spectroscopy and thermogravimetric analysis; both these techniques, also, demonstrated that the functionalization occurs only on the external surface of HNT. Turbidimetric and DLS analyses showed that the introduction of ionic liquid on the HNT surface causes the formation of aggregates. SEM investigations showed that the tubular shape of the nanoclay is not lost upon the grafting of the organosilane and the binding of the IL.

A preliminary study in catalytic field of the material employed as support for Palladium particles, demonstrated that the catalyst is efficient in the Suzuki reaction.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2013.10.044>.

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