PAPER

Design of PNIPAAM covalently grafted on halloysite nanotubes as a support for metal-based catalysts†

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A thermo-responsive polymer such as poly(*N*-isopropylacrylamide) (PNIPAAM) was covalently grafted on the external surface of halloysite nanotubes (HNTs) by means of microwave irradiation. This nanomaterial was used as a support and stabilizer for palladium nanoparticles. The obtained HNT–PNIPAAM/PdNPs was characterized by means of TGA, SEM, EDS and TEM analyses. The palladium content of the catalyst was estimated to be 0.4 wt%. The stability of the catalytic material at different temperatures (below and above the PNIPAAM lower critical solution temperature) was tested in the Suzuki reaction under microwave irradiation. In addition, TEM analysis after five consecutive runs was performed. The catalyst showed a good catalytic activity toward the Suzuki cross-coupling reaction between phenylboronic acid and several aryl halides in aqueous media under microwave irradiation and low palladium loading (0.016 mol%, 8 μg of Pd). Turnover numbers (TONs) and frequencies (TOFs) up to 6250 and 37 500 h^{-1}, respectively, were reached. The catalyst was easily separated from the reaction mixture by centrifugation and reused for five consecutive cycles with a small drop in its catalytic activity.

Introduction

Halloysite nanotubes (HNTs) are natural alumino-silicate nanomaterials with a unique combination of hollow tubular nanostructure, large aspect ratio, suitable mechanical strength, high perspectives in terms of functionality, biocompatibility and wide availability.[1] Moreover, their low cost makes them an attractive alternative to the better known carbon nanotubes. As a consequence, in the past years, HNTs have garnered particular interest in materials science. HNTs possess different inner and outer surface compositions; in particular most of the aluminol groups are located in the halloysite inner surface, whereas the external portions are mainly composed of siloxanes, providing a surface available for covalent grafting of organic moieties.[2]

This peculiar chemical composition allows different functionalization methods of both surfaces that increase the HNTs application fields.[3,4] In this context, being biocompatible nanomaterials,[5,6] HNTs are mainly employed for the encapsulation of biologically active molecules,[7–9] biomedical implants[10,11] and controlled drug delivery.[12] Furthermore, thanks to their structural features, HNTs are suitable for a potential application as support for catalytic composites. Various catalysts loaded on the HNTs with excellent catalytic

performance have been reported.[13–15] Gold nanoparticles (NPs) were successfully loaded on halloysite[16] and the obtained Au/HNTs hybrid showed high catalytic activity for solvent-free oxidation of benzyl alcohol.[17]

Using clays with tube morphology was beneficial for improving dispersibility and photocatalytic activity of TiO$_2$-NPs.[18,19] Yang *et al.* reported palladium NPs deposited on HNTs for hydrogenation of styrene with enhanced catalytic activity.[20]

Recently, we reported the synthesis of novel palladium-based catalytic systems using halloysite nanotubes modified with imidazolium or triazolium moieties as supports for PdNPs and we successfully employed these supported catalysts in the Suzuki reaction under microwave irradiation.[21,22]

Stimuli-responsive polymer materials are playing an increasingly important role in catalysis, since catalytic reactions can be controlled by tuning appropriate stimuli.

Poly(*N*-isopropylacrylamide) (PNIPAAM) hydrogel is one of the most popular thermoresponsive polymers known. It shows a dramatic volume phase transition at the lower critical solution temperature (LCST) around 32 °C, above which it undergoes dehydration and phase separation. The swelling of PNIPAAM hydrogels is mainly due to changes in the hydrogen bonding of the PNIPAAM network with water molecules. At a temperature above LCST, some of the hydrogen bonds are dissociated, and the hydrophobic interactions among the hydrophobic groups in the PNIPAAM network are dominant.[23] This causes the release of water molecules trapped in the network, causing the hydrogel collapse. PNIPAAM due to its thermo-responsive nature can be loaded or combined with metal particles in order to prepare

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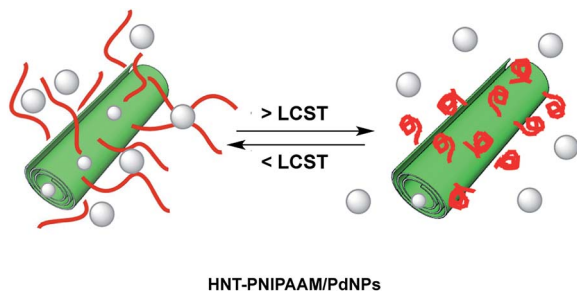
Fig. 1 Cartoon representation of swelling behaviour of HNT–PNI-PAAM/PdNPs.

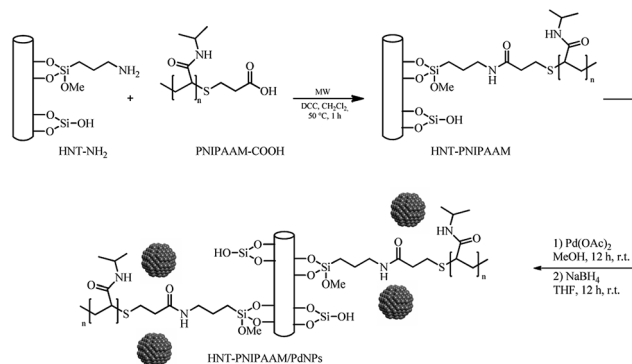**Scheme 1** Schematic representation of the synthesis of HNT–PNI-PAAM/PdNPs catalyst.

"smart catalysts" that show improved catalytic activities by adjusting the temperature below or above the LCST. In this context several PNIPAAM based catalysts employed for the hydrodechlorination of 4-chlorophenol, the reduction of 4-nitrophenol or catalytic wet hydrogen peroxide oxidation of phenol are reported.[24] Moreover, since PNIPAAM can selectively provide hydrophilic or hydrophobic nano-environments by simply changing the temperature of the reaction medium, it is possible to carry out Suzuki reaction in water under green conditions using PdNPs supported on this polymer. For example, PNIPAM-*co*-4-vinylpyridine support was used for palladium immobilization and used in Suzuki cross-coupling with excellent results without Pd leaching.[25]

To best of our knowledge, up to date only few examples on halloysite nanotubes dispersed in PNIPAAM aqueous solution are reported.[26] HNT/PNIPAAM hydrogels were used as photo-catalysts[27] as well as catalyst supports for palladium NPs in the Suzuki reaction.[28]

Herein we report an efficient strategy to prepare HNTs-based catalyst through direct chemical grafting with stimuli-responsive polymer (PNIPAAM) coordinating PdNPs (Fig. 1). The HNT–PNIPAAM/PdNPs was tested as catalyst in the Suzuki reaction under microwave irradiation. The use of microwave irradiation provides a rapid, direct and consistent energy for the cross coupling reactions, therefore it had beneficial effects on the efficiency of the Suzuki reactions increasing the reaction rates.

Results and discussion

The HNT–PNIPAAM material was synthesized by randomly covalent grafting of the carboxylic acid-terminated PNIPAAM to halloysite nanotubes as previous reported by us (Scheme 1).[29] Furthermore, in order to reduce reaction time, we performed the same reaction under microwave irradiation for 1 h, at temperature of 50 °C, using CH_2Cl_2 as solvent. After work up, the obtained nanomaterial was analysed by thermogravimetric analysis (TGA) which confirmed the formation of HNT–PNI-PAAM nanomaterial and allowed to calculate the loading percentage of PNIPAAM attached on the HNT surface, which was 13 wt%. It is noteworthy that just 1 h of MW irradiation is enough to obtain a loading of polymer on the HNT external

surface that approaches to the previously reported by us[29] in traditional conditions, which take 72 h.

The immobilization of palladium nanoparticles on the support was achieved by solubilizing $Pd(OAc)_2$ in a mixture of HNT–PNIPAAM in methanol. The solid material was recovered by filtration and, finally, the Pd(II) species were reduced to Pd^0 with $NaBH_4$ in tetrahydrofuran. The content of palladium nanoparticles was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and was estimated as 1.3 wt%.

The presence of palladium species in the structure of the HNT–PNIPAAM/PdNPs catalyst was confirmed by energy-dispersive X-ray spectroscopy (EDS) obtained from SEM analysis (Fig. 2). EDS experiment was useful to determine the palladium loading of the catalytic system that was of 1.3 wt% accordingly to ICP-OES analysis.

EDS measurements further confirmed the successful functionalization highlighting the presence of sulfur in the structure of the nanomaterial deriving from the covalently grafted polymer. SEM micrographs (Fig. 3) showed that the characteristic lengths and the tubular shape of HNTs were preserved in the PNIPAAM–HNT/PdNPs catalyst.

According to the TEM images (Fig. 4), HNT–PNIPAAM/PdNPs catalyst shows the typical rod-shaped structure of HNTs with
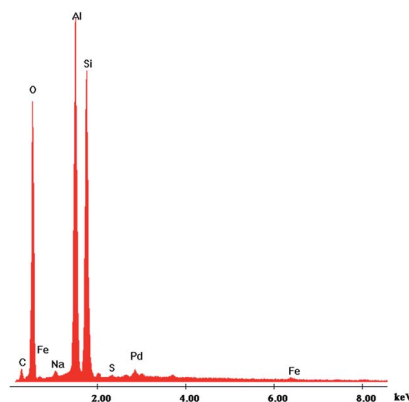

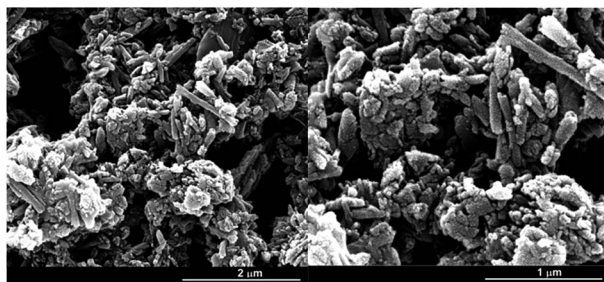**Fig. 2** EDS image of HNT–PNIPAAM/PdNPs catalyst.
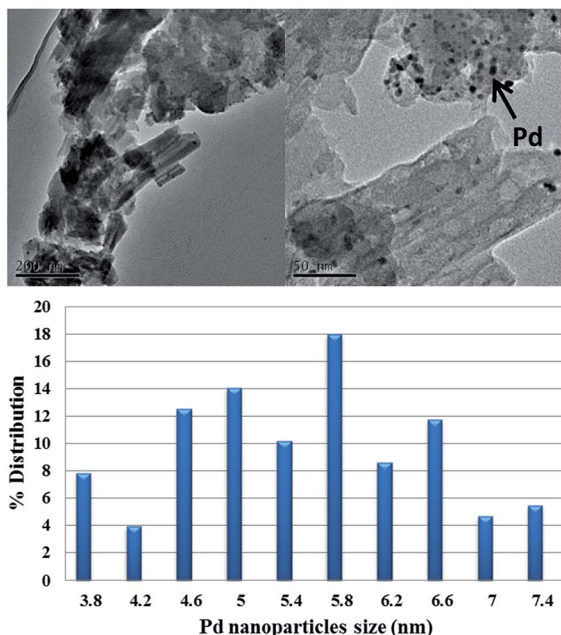
Fig. 3 SEM images of the HNT−PNIPAAM/PdNPs catalyst.

Fig. 4 TEM images of the HNT−PNIPAAM/PdNPs catalyst.

a diameter of about 100 nm and a length of about 0.7 μm. The Pd nanoparticles were mainly immobilized on the surface and also anchored to the interlayer of HNTs, having spherical morphologies with diameters of about 5.5 ± 1.0 nm (number of counts (n) = 128).

The catalytic activity of the HNT−PNIPAAM/PdNPs nanomaterial was evaluated in Suzuki–Miyaura coupling reaction. In particular our studies were focused on determining the influence of temperature and amount of catalyst on the reaction. In order to find the best experimental conditions, the reaction of 4-bromoacetophenone with phenylboronic acid was selected as model. Based on our previous studies on Suzuki reaction, with the aim to better solubilize both organic substrate and inorganic base (K_2CO_3), we carried out the catalytic tests in a water/ethanol mixture (50% v/v).

As shown in Table 1, excellent results were obtained in all cases, and no byproducts were detected. Thus, the conversions reported correspond to the reaction yields.

To verify the HNT−PNIPAAM/PdNPs stability and its thermo-responsive behaviour, the title Suzuki reaction was carried out

Table 1 Optimization of experimental conditions for Suzuki cross-coupling reaction under microwave irradiation

Entry	T (°C)	Conv.[a] (%)
1	25	17
2	50	95
3	120	>99
4[b]	120	>99

[a] Determined by ^{1}H-NMR (Fig. S1–S4). [b] Reaction conditions: H_2O/EtOH (1 : 1) 1.2 mL, catalyst 0.016 mol%, 2 mg.

in a different temperatures ranging between 25 and 120 °C, under microwave irradiation. Catalyst was recovered by centrifugation and was reused in the same reaction for five runs (Fig. 5). When recycling tests were carried out at temperature above the LCST, catalyst afforded the desired biphenyl-4-acetophenone product in good yields after four runs ranging from 99 to 77%. However, in the 5th run we observed a decreased yield (50%). The amount of Pd nanoparticles released into solution during the reaction was determined by ICP-OES, which was less than 1 wt%. The absence of leaching of palladium has been attributed to a "release and catch" mechanism.[30] It has been proposed that Suzuki cross-coupling can involve the presence of soluble palladium species (leaching) arising from the surface of the catalyst. However, after completion of the catalytic process, palladium is redeposited onto the support avoiding the leaching in solution.

To confirm the above mentioned mechanism additional experiments were carried out. In three parallel reactions (4-bromoanisole and phenylboronic acid) the catalyst was filtered-off after 1 min of microwave irradiation. In the first one, the reaction was stopped and the crude product was analysed by ^{1}H-NMR. In this case we observed a conversion of 96% of the
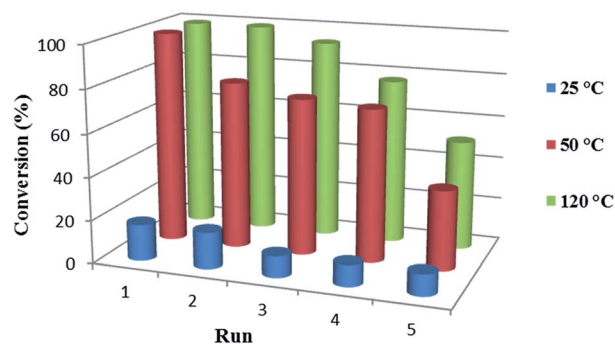

Fig. 5 Effect of temperature on the Suzuki reaction between 4-bromoacetophenone and phenylboronic acid (reaction condition: MW, phenylboronic acid (0.547 mmol), 4-bromoacetophenone (0.55 mmol), K_2CO_3 (0.615 mmol), EtOH/H_2O 1 : 1 (1.2 mL), catalyst (0.16 mol%, 7 mg)).

correspondent biaryl derivative. The second reaction was quickly filtered still hot (hot filtration) and left to stir (without any catalyst) for further 9 min leading to a total conversion (>99%). Conversely, the last reaction, which was cooled down to rt prior filtration and reacted for 9 min (cold filtration), showed no extra conversion, actually we observed a decrease (70%), probably due to the degradation of reactants and products caused by the prolonged microwave irradiation. To further confirm the release and catch mechanism an additional reaction was carried out as follow. The catalyst was treated at 120 °C for 3 min under microwave irradiation in a mixture H_2O/EtOH 1 : 1. It was filtered still hot and to the solution obtained were added the reactants (4-bromoanisole and phenylboronic acid) and the Suzuki reaction was performed for 10 min in the experimental conditions described above. In this way we obtained a 12% of conversion, confirming the presence of soluble Pd species in solution released from the catalyst at high temperature.

On the contrary, as expected for the thermo-responsive behaviour (LCST < 32 °C), at 25 °C very low conversions (about 10%) were observed and, also in this case ICP-OES analysis showed no palladium leaching during the course of Suzuki reaction. Interestingly, when the catalyst was reused, after recovering, in the same reaction at 50 °C, an increase in the conversion (34%) was observed.

The difference of catalytic activity of HNT–PNIPAAM/PdNPs at different temperatures can be attributed to the thermo-responsive behaviour of PNIPAAM grafted onto halloysite surface. At room temperature, the PNIPAAM chains should adopt an extended conformation forming a hydrophilic nano-environment. Therefore, the Suzuki reaction, with hydrophobic substrates, such as 4-bromoacetophenone, is unsatisfactory and the yields are low (Fig. 5). Above the LCST the PNIPAAM chains collapse to form a dense layer covering HNT surface; the grafted PNIPAAM brushes become hydrophobic, facilitating the mass-transfer of hydrophobic substrates and promoting the cross coupling process.[31] As a result, we observed higher conversions at temperature above the LCST.

Such temperature-responsive behaviour was reversible, as the recycled catalyst showed the same activity and thermo-responsive behaviour. The influence of temperature in catalytic process was already reported in literature for PNIPAAM@SBA systems.[32]

To explain the drop of catalytic activity after five runs carried out above the LCST, we performed TEM analysis keeping in mind that Pd^0 nanoparticles have the tendency to agglomerate during the catalytic cycles. This experiment (Fig. 6) revealed agglomeration of Pd nanoparticles (mean diameter 6.6 ± 1.2 nm, $n = 128$) on the surface of HNTs, furnishing a possible explanation for the drop of the catalytic activity due to the reduction in the surface area and saturation of the coordination sites.[33] This could be explained by the Ostwald ripening favoured under the harsh catalytic reaction conditions used. After catalytic process, the small soluble Pd species leached by the catalyst surface, as above mentioned, are redeposited on the support forming larger and less reactive Pd clusters.[34]

In the last years the use of water as reaction medium for coupling reaction catalyzed by heterogeneous palladium
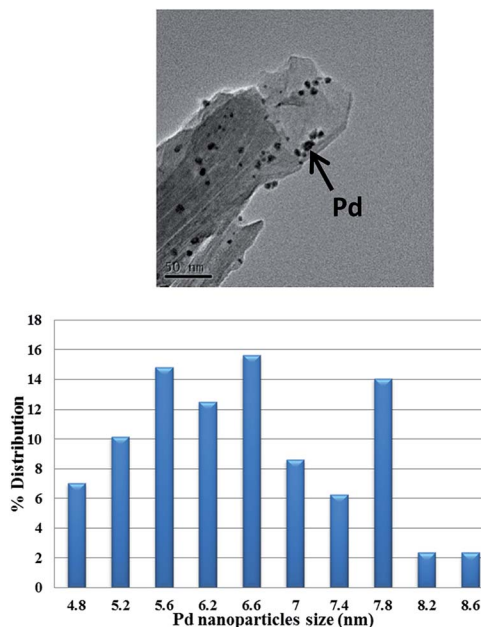

Fig. 6   TEM image of HNT–PNIPAAM/PdNPs material after five catalytic runs.

catalyst has received considerable attention due to the rising concerns for the environment being that water is cheap, environmental friendly, and allows simple separation and catalyst recycling.

With this idea in mind, we decided to perform the Suzuki coupling reaction in water, using K_2CO_3 as base and under microwave irradiation. An accurate screening of the reaction condition was carried out choosing the coupling between 4-bromoacetophenone and phenylboronic acid as reaction model.
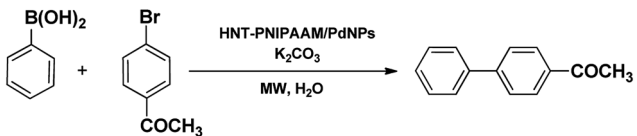
In order to obtain the best combination the influence of different parameters, namely reaction time, temperature, catalyst concentration as well as the addition of a transfer phase additive (Table 2), were examined. In the most of the cases the conversions reported in Table 2 correspond to yields. The better results were obtained with an irradiation time of 10 min and at 120 °C (entry 4). It is worth to note that even though 15 min of irradiation lead to higher conversions, however we observed a decrease in the yield (entry 5). Prolonged irradiation, indeed, causes decreased in conversions (entries 3–8) and yields (entry 5) probably due to the formation of by-products such as the homocoupling and the dehalogenation products or degradation of both reactants and products.[35]

The use of a transfer phase additive, such as tetrabutylammonium bromide (TBAB), even in low amount, accelerated the reaction (entry 6) since it facilitated the dissolution of the organic reactants in the water phase. Then we decided to further reduce the amount of catalyst down to 0.016 mol%, obtaining quantitative conversion (entry 9).

The scope of Suzuki cross coupling reactions was investigated using phenylboronic acid and a broad range of aryl halides under the optimized conditions. The reactions of differently substituted aryl halides and phenylboronic acid were

Table 2 Optimization of experimental conditions for Suzuki cross-coupling reaction under microwave irradiation

Entry	Pd (mol%)	Additive	t (min)	T (°C)	Conv.[a] (%)
1	0.16	—	10	70	20
2	0.16	—	15	70	36
3	0.16	—	30	70	20
4	0.16	—	10	120	67
5	0.16	—	15	120	85 (55)[c]
6	0.16	TBAB[b]	2	120	90
7	0.16	TBAB[b]	10	120	>99
8	0.16	TBAB[b]	15	120	93
9	0.016	TBAB[b]	10	120	>99

[a] Determined by ^{1}H-NMR (Fig. S5–S13). [b] Reaction conditions: H_2O (1.2 mL), tetrabutylammonium bromide 0.05 mmol. [c] Yield (%).
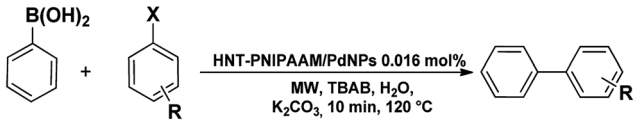
carried out in presence of K_2CO_3 (1.12 eq.), TBAB as additive (0.05 mmol) and 0.016 mol% (0.7 mg) of HNT–PNIPAAM/PdNPs catalyst using water as solvent. The reactions were heated at 120 °C for 10 min under microwave irradiation.

Conversions were high, ranging from 73% to 99%; in all case no byproducts were detected and the conversions reported in Table 3 correspond to yields.

The less reactive aryl chlorides gave no or very low conversions (entries 9 and 10) under the same reaction conditions.

The obtained good results could be due, once again, to the thermo-responsive behavior of PNIPAAM.

Table 3 Suzuki cross-coupling reaction of phenylboronic acid with various aryl halides under optimized reaction conditions under microwave irradiation

Entry	Ar–X	Conv.[a] (%)	TON[b]	TOF[c] (h^{-1})
1	4-Bromoacetophenone	>95	6250	37 500
2	4-Iodoanisole	85	5310	31 870
3	4-Bromobenzaldheyde	94	5880	35 250
4	4-Bromoanisole	85	5310	31 880
5	3-Bromobenzaldheyde	82	5130	30 750
6	3-Bromoanisole	64	4000	24 000
7	4-Iodoacetophenone	94	5880	35 250
8	2-Iodotoluene	73	4560	27 380
9	4-Chlorobenzaldheyde	—	—	—
10	1-Chloro-4-nitrobenzene	4	250	1500

[a] Determined by ^{1}H-NMR (Fig. S13–S21). [b] Turnover number (TON) calculated as moles of substrate converted/moles of palladium. [c] Turnover frequency (TOF) calculated as TON/hours.

The grafted PNIPAAM brushes, indeed, become hydrophobic and collapse on the HNT surface at temperature above the LCST, and therefore could provide a nano-environment for hydrophobic guest molecules in water.

These results demonstrate the good catalytic activity of HNT–PNIPAAM/PdNPs in microwave promoted Suzuki cross-coupling reaction at 120 °C with turnover numbers (TONs) up to 6250 and turnover frequencies (TOFs) up to 37 500 h^{-1}.

The recycling ability of this novel supported palladium catalyst was also investigated. For this purpose the microwave assisted Suzuki cross coupling reaction of 4-bromoacetophenone with phenylboronic acid under the optimized reaction conditions was studied. Because of the very small amount of catalyst used (0.7 mg), we carried out recycling investigations using catalyst at 0.07 mol% (3 mg).

After each cycle, the catalyst was recovered by centrifugation, washed with diethyl ether and water and directly used for the next cycle. The catalyst showed to be recyclable for five consecutive times. The activity slightly dropped in the run 3 yielding 85% conversion and further dropped in run 5 to 70% (Fig. 7). In order to determine the degree of leaching of the metal from the heterogeneous catalyst, the palladium content of the supernatant, after each cycle of washing, was determined by ICP-OES and no leaching was detected. Thus the catalytic activity dropped to some extent after the 5th cycle and it could be ascribed to agglomeration of Pd nanoparticles on the surface of HNT–PNIPAAM, as above mentioned.

It could be noteworthy to compare the performance of the HNT–PNIPAAM/Pd catalyst with other supported Pd nanoparticle catalysts developed for Suzuki cross coupling reactions. Several studies reported Pd nanoparticles stabilized by hybrid polymeric materials used as catalysts in Suzuki reactions.[36–38] Among them Pd nanoparticles were stabilized by polyvinyl pyrrolidone (PVP), polystyrene–polyethylene oxide and poly(amido-amine) dendrimers as well as other polymers.[38,39]

However some nanocatalysts have shown limited catalytic activity such as lower product yields using low catalyst loadings, no recyclability and low TON and TOF values.[38] For example, catalysts based on Pd supported on PVP afforded the Suzuki products, under microwave irradiation, in 75–79% and 43–87% yields for aryl iodides and bromides, respectively.[40]
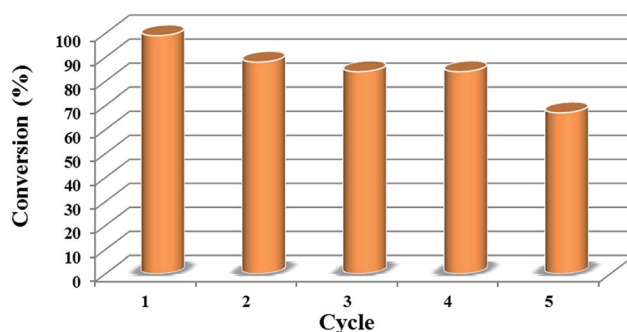

Fig. 7 Recycling investigations (reaction condition: MW, 10 min, 120 °C, phenylboronic acid (0.547 mmol), 4-bromoacetophenone (0.550 mmol), K_2CO_3 (0.615 mmol), H_2O (1.2 mL), TBAB (0.05 mmol), catalyst (0.07 mol%, 3.0 mg)).

Furthermore the Suzuki reactions of aryl iodides and bromides were carried out by microwave irradiation using higher Pd/poly(*N*,*N*-dihexylcarbodiimide) catalyst loadings (0.5 mol%) that could be recycled up to five times with slightly decreased activity.[41] Recently, thermo-responsive polymers have been used as both stabilizer and support for the Pd nanoparticles and resulted in highly recyclable catalysts for the Suzuki coupling of several aryl halide and phenylboronic acid.[28] On the basis of these examples, it can be concluded that the current HNT–PNIPAAM/Pd material provides highly stable and efficient catalysts for cross coupling reactions as compared to other Pd nanoparticles stabilized by polymeric molecules.

Experimental section

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

Halloysite (from Sigma-Aldrich) has an average tube diameter of 50 nm and inner lumen diameter of 15 nm. Typical specific surface area of this halloysite is 65 m^2 g^{-1}; pore volume of 1.25 mL g^{-1}; refractive index 1.54; and specific gravity 2.53 g cm^{-3}. HNT-NH$_2$ was synthesized as previously reported.[29]

Thermogravimetric analyses were performed by a Q5000 IR apparatus (TA Instruments) under a nitrogen flow of 25 cm^3 min^{-1} for the sample and 10 cm^3 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}.

The microscope ESEM FEI QUANTA 200F with EDX probe was used to study the morphology and elemental analysis of the HNT–PNIPAAM. 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 syntheses were carried out with a CEM DISCOVER monomode system in closed vessel.

^{1}H NMR spectra were recorded at 300 MHz in CDCl$_3$ solutions at room temperature on a Bruker 300 MHz spectrometer.

TEM micrographs were acquired with a Jeol JEM 2100 microscope operating at 200 kV. A drop of each dispersion has been deposited in a 3 mm nickel grid holey carbon coated (Taab). The grid was dried overnight before observation. No coating was applied for TEM observation.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analyses were carried out with an Optima 2100, Perkin Elmer, equipped with an auto sampler model AS-90. Analyses were conducted using a calibration curve, obtained by dilution (range: 0–10 ppm) of palladium standard solution for ICP-OES analyses. The operative wavelengths were 340.458 and 363.470 nm.

Synthesis of HNT–PNIPAAM *via* MW

PNIPAAM (94 mg, 10 equiv.), *N*,*N*-dicyclohexylcarbodiimide (DCC) (88 mg, 10 equiv.) and CH$_2$Cl$_2$ (1 mL) were placed in a microwave test tube provided with a cap. The mixture was stirred under argon atmosphere, at room temperature for 10 min. Afterward HNT-NH$_2$ (500 mg) was quickly added. Then, the mixture was inserted into microwave apparatus setting a temperature of 50 °C and under constant stirring for 60 min, then filtered under reduced pressure, washed whit H$_2$O and dried overnight under reduced pressure at room temperature.

Typical procedure for the synthesis of the palladium catalysts

In a 50 mL round bottom flask were placed HNT–PNIPAAM (100 mg), Pd(OAc)$_2$ (10 mg, 0.0445 mmol) and MeOH (20 mL). The obtained dispersion was sonicated for 1 min and was stirred for 18 h at room temperature. The mixture was filtered under reduced pressure, washed three times with 20 mL MeOH and dried under reduced pressure at room temperature. The material was re-suspended in THF (20 mL) and to this suspension NaBH$_4$ (10 mg, 0.264 mmol) as a reducing reagent was added. The suspension was stirred at room temperature for 18 h. MeOH (10 mL) was added to destroy the NaBH$_4$ residual, then filtered under reduced pressure, washed whit 20 mL of MeOH and 20 mL of THF and then dried overnight under reduced pressure at room temperature.

Typical procedure for the Suzuki reaction *via* microwave irradiation

HNT–PNIPAAM/PdNPs catalyst (0.16 mol% or 0.016 mol%), phenylboronic acid (65 mg, 0.547 mmol), K$_2$CO$_3$ (84 mg, 0.61 mmol), aryl bromide (0.550 mmol), H$_2$O/EtOH (50% v/v) (1.2 mL) or water (1.2 mL) were placed in a microwave pressurized test tube provided with a sealed cap. The mixture was inserted into microwave apparatus setting a temperature of 120 °C (14 W), 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–PNIPAAM/PdNPs catalyst (3 mg, 0.07 mol%), phenylboronic acid (65 mg, 0.547 mmol), K$_2$CO$_3$ (84 mg, 0.615 mmol), 4-bromoacetophenone (0.55 mmol), a mixture of H$_2$O/EtOH (1 : 1) (1.2 mL) or water (1.2 mL) were placed in a microwave pressurized test tube provided with a sealed cap. The mixture was inserted into microwave apparatus setting a temperature of 120 °C (14 W), under constant stirring for 10 min. The reaction mixture was then centrifuged and the supernatant was decanted; the residual solid was washed with CH$_2$Cl$_2$, Et$_2$O and water. HNT–PNIPAAM/PdNPs was dried and reused.

Conclusions

In conclusion, we have covalently linked PNIPAAM thermo-responsive polymer on halloysite external surface by a simple synthetic route. The HNT–PNIPAAM nanomaterial was used as support and stabilizer of palladium nanoparticles. EDS analysis and TEM images confirmed the presence of Pd on the support, whereas SEM images showed that upon palladium immobilization the tubular shape of halloysite was preserved. The catalyst stability at varying temperatures in the Suzuki reaction was tested. TEM analysis after five consecutive runs showed Pd agglomeration.

The catalytic performance of this hybrid material was tested in Suzuki cross-coupling reaction of aryl halides with phenylboronic acid in aqueous media under microwave irradiation. The good catalytic activity was also demonstrated by the low amount of catalyst employed (just 0.016 mol%, 2.34 mg) and high TON and TOF values. Furthermore, the catalyst showed good recyclability for five cycles with negligible Pd leaching.

Acknowledgements

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