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Hydrotalcite-supported palladium nanoparticles as catalysts for the Suzuki reaction of aryl halides in water

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ABSTRACT

A simple protocol for the Suzuki reaction of aryl halides with phenylboronic acid is proposed. The catalyst used consists of Pd(0) nanoparticles supported on an Mg/Al hydrotalcite. The catalyst was prepared and characterized in this work for the first time. Supported nanoparticles were obtained by depositing a Pd(II) salt onto the support and subsequently reducing it to Pd(0). The greatest novelties of the synthetic process are the use of a hydrogen donor (cyclohexene) to reduce the palladium precursor salt and that of water as solvent in the Suzuki reaction. Biphenyl conversions in the Suzuki reaction of phenylboronic acid with iodobenzene, bromobenzene and chlorobenzene were all excellent, and quantitative yields obtained within a very short time. Even fluorobenzene provided excellent results improving on many reported values for chelated Pd homogeneous catalysts. No homocoupling reaction was detected; also, although homogeneous and heterogeneous catalysis coexist, the catalyst can be recovered for reuse with no loss of activity.

1. Introduction

The Suzuki cross-coupling reaction —or simply, Suzuki reaction— between an aryl halide and phenylboronic acid is widely used in modern organic syntheses. In its simplest form, the process involves the formation of a biphenyl molecule by coupling of an aryl halide or triflate to phenylboronic acid in the presence of a palladium catalyst (see Scheme 1) [1].

According to Kim and Yu [2], the multistep mechanism for this reaction involves aromatic nucleophilic substitution (S_NAr); as a result, iodo- and bromoarenes are among its most common substrates. Especially active catalysts have enabled the use of chlorinated substrates under similar conditions with excellent conversion and selectivity results [3–7]. By contrast, fluorinated derivatives have scarcely been used in the Suzuki reaction owing to their high cost relative to their chlorinated counterparts and the low reactivity of the C—F bond in S_NAr processes, which requires using more drastic conditions. There are few references to Suzuki reactions involving aryl fluorides. In most cases, the substrate contained aromatic rings with strong electron-withdrawing substituents capable of triggering their activity in S_NAr reactions [2,8–10]; in virtually all, the catalyst was a homogeneous Pd complex and the reaction medium an organic solvent.

In recent years, supported Pd nanoparticles have provided excellent results as catalysts for the Suzuki reaction [11–14]. Their success lies in the combination of nanoparticles and a suitable support providing catalysts with special properties and an enormous catalytic potential.

This paper reports the synthesis of a catalyst consisting of palladium nanoparticles supported on a hydrotalcite and its use in the Suzuki reaction of aryl halides including fluorobenzene with phenylboronic acid under environmentally benign conditions provided by the use of water as solvent. One important novelty of the proposed procedure is that the Pd(II) precursor salt used to obtain the Pd(0) nanoparticles is reduced with a hydrogen donor (the hydrocarbon cyclohexene) (see Scheme 2). Previously reported Pd(0) nanoparticle catalysts were obtained by using other reductants such as sodium borohydride [15,16], hydrazine [17] or even molecular hydrogen [4].

Hydrotalcite-like compounds —or, simply, hydrotalcites— are a class of anionic clays also known as “layered double hydroxides” the great potential of which in a number of scientific fields has aroused much interest in recent years [18–20]. Structurally, hydrotalcites are similar to brucite, $Mg(OH)_2$, except that some Mg^{2+} ions are replaced by trivalent metals of a similar ionic radius [21,22]. This introduces a charge deficiency which causes

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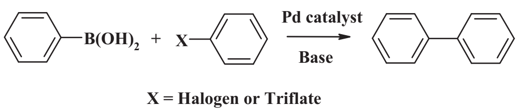
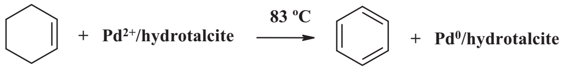


Scheme 1. General process for Suzuki cross-coupling reaction.



Scheme 2. Reduction of Pd^{2+} with cyclohexene as hydrogen donor.

brucite-like layers to be positively charged. Restoring electroneutrality requires the insertion of an appropriate anion [19] in addition to crystallization water in the interlayer region (Fig. 1). The parent hydrotalcite-like compound is the natural mineral hydrotalcite, of formula $Mg_6Al_2(OH)_2CO_3{\cdot}4H_2O$. Magnesium ion can be exchanged both with trivalent cations and with divalent ones [21,22]. The general formula of hydrotalcites is thus $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/m}]^{m-}{\cdot}nH_2O$, where M(II) and M(III) are a divalent and trivalent metal, respectively, at octahedral positions of Mg^{2+} in brucite-like layers and A is the interlayer anion—which can vary widely in nature and be either inorganic or organic. x, which is defined as the ratio M(II)/[M(II) + M(III)], typically ranges from 0.17 to 0.33, which corresponds to an M(II)/M(III) ratio of 2–4 [9].

2. Experimental

2.1. Preparation of the catalyst

The hydrotalcite used was prepared by using a coprecipitation method described elsewhere [23]. In a typical synthetic run, a solution containing 0.3 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.15 mol of $Al(NO_3)_3{\cdot}9H_2O$ in 250 mL of de-ionized water was used (Mg/Al = 2). This solution was slowly dropped over 500 mL of a Na_2CO_3 solution at pH 10 at 60 °C under vigorous stirring. The pH was kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was kept at 80 °C for 24 h, after which the solid was filtered and washed with 2 L of de-ionized water. The hydrotalcite thus prepared was ion-exchanged with carbonate to remove nitrate ions intercalated between layers. The procedure involved suspending the solids in a solution containing 0.345 g of Na_2CO_3 in 50 mL of bidistilled, de-ionized water per gram of hydrotalcite at 100 °C for 2 h. Then, each solid was filtered off in vacuo and washed with 200 mL of bidistilled, de-ionized water. The new hydrotalcite thus obtained was subjected to further ion-exchange under the same conditions. The resulting Mg/Al solid, named HT, was used to support Pd^{2+} by deposition from an N,N-dimethylformamide suspension containing the amount required to ensure that the final catalysts would include 0.75% of Pd by weight. After the suspension was stirred at room temperature for 24 h, the solvent was evaporated to dryness and the residual solid dried in a stove at 120 °C. The resulting solid, named HT-Pd(II), was reduced to Pd(0) with the hydrocarbon cyclohexene as hydrogen donor. To this end, an amount of 1 g of pre-catalyst was refluxed with 10 mL of cyclohexene at 83 °C for 1 h. Under these conditions, cyclohexene was converted into benzene and hydrogen released in the reaction reduced impregnated Pd^{2+} to Pd^0 (see Scheme 2). After the mixture was cooled, the catalyst, labelled HT-Pd(0), was filtered off and washed with cyclohexane and methanol.

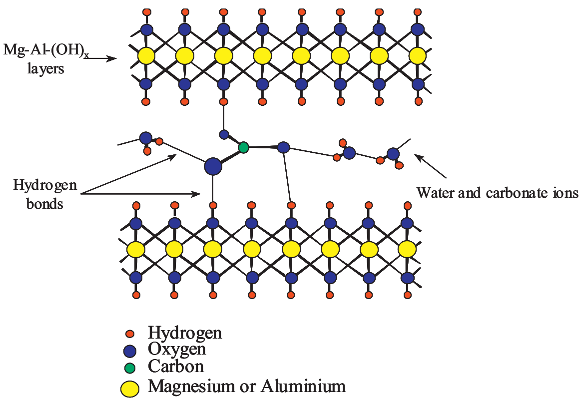


Fig. 1. Structure of hydrotalcite.

2.2. Characterization of the catalysts

The Mg/Al ratio in the hydrotalcite and the amount of Pd deposited on it were determined by inductively coupled plasma mass spectrometry (ICP-MS) on an ELAN DRC-E Perkin Elmer ICP-MS instrument under standard conditions. BET surface areas were calculated from nitrogen adsorption–desorption isotherms obtained at −196 °C on a Micromeritics ASAP 2010 instrument. Samples were outgassed in vacuo at 100 °C for 12 h prior to use. All solids [HT, HT-Pd(II) and HT-Pd(0)] were checked for crystallinity by X-ray diffraction (XRD) analysis. Powder patterns were recorded on a Siemens D-5000 diffractometer using CuK_α radiation over the range 5–80°. Particle size and external morphology of the samples were examined with a JEOL JEM2010 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) measurements were made on an Escalab 210 spectrophotometer, using pellets 13 mm in diameter that were obtained by pressing at a low pressure. Because of the sample dimensions, experiments were conducted in the large-area XPS (LAXPS) mode. A double-anode X-ray gun at an average power of 100 W (10 kV × 10 mA) was used for this purpose. Vacuum in the main chamber was always better than 6×10^{-9} mbar. Raman spectra for the solids were acquired with a Renishaw Raman instrument (InVia Raman Microscope) equipped with a Leica microscope furnished with various lenses, monochromators and filters, and a CCD. Spectra were obtained by excitation with green laser light (532 nm) from 500 to 800 cm^{-1}. A total of 128 scans per spectrum were performed in order to improve the signal-to-noise ratio.

2.3. Suzuki reaction

The Suzuki cross coupling reaction was conducted in a 25 mL two-neck flask at 100 °C containing 1.5 mmol of phenylboronic acid, 0.99 mmol of arylhalide, 5 mL of water, 1.98 mmol of potassium carbonate, 75 mg of sodium dodecylsulphate and 0.02 mmol (2.13 mg) of Pd. The system was stirred throughout the process. The resulting products were identified from their retention times by GC/MS analysis.

3. Results and discussion

3.1. Characterization of catalysts

The elemental analysis performed by using ICP methodology revealed that the Mg/Al ratio in both the starting hydrotalcite, Pd(II) pre-catalyst and Pd(0) catalyst was 2.03, and also that the Pd content of the latter two was 0.6 wt% (see Table 1). Therefore, solid HT had an Mg/Al ratio identical with the theoretical value. Also, such a metal ratio was preserved in the pre-catalyst and catalyst obtained from the hydrotalcite. These results suggest that Mg and Al cations were virtually completely incorporated into the solid phase.

Hydrotalcite HT has a surface area of about 78 m^2/g. When palladium is loaded into this hydrotalcite, to obtain solid HT-Pd(II), a

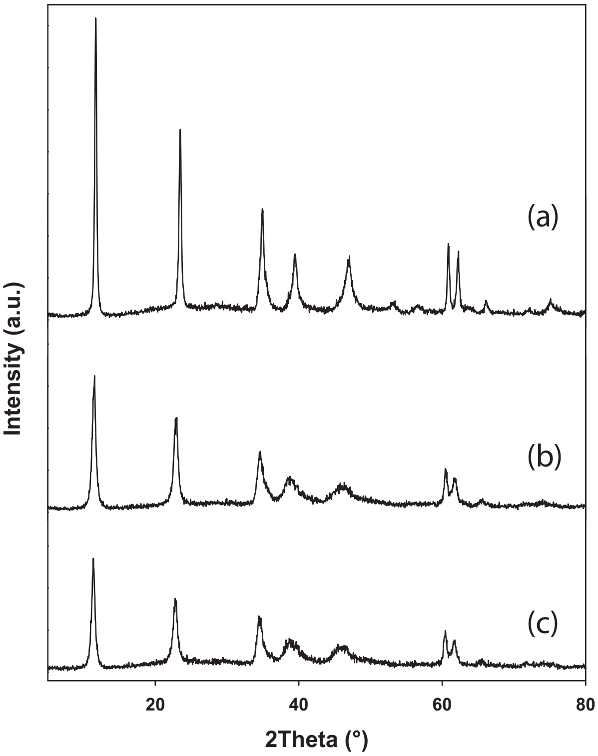


Fig. 2. XRD diffraction patterns for HT (a), HT-Pd(II) (b) and HT-Pd(0) (c).

decrease in surface area is observed, 58 m^2/g. Finally, after reduction to obtain the catalyst HT-Pd(0), the surface area remains constant, 61 m^2/g. This decrease may be due to pore blocking. These results are shown in Table 1.

Fig. 2 shows the XRD patterns for the hydrotalcite, pre-catalyst, solid HT-Pd(II) and the catalyst [HT-Pd(0)]. All patterns are typical of a layered material. The strongest signal ($2\theta \sim 11°$), corresponding to the (0 0 3) crystallinity indices, was used to determine the lattice distance, d_{003}. This in turn was used to calculate parameter c ($c = 3 \times d_{003}$), which was found to be 2.27 nm. Thus, the interlayer distance in HT was 0.76 nm, which is consistent with reported values for hydrotalcites with a metal ratio close to 2 containing carbonate ion in their interlayer region [24]. A comparison of the XRD patterns for HT with those for the pre-catalyst (Fig. 2b) and catalyst (Fig. 2c) revealed the absence of substantial differences; this suggests that interlayer carbonate ions were not exchanged with chloride ions from the palladium precursor. There was, however, a difference in signal intensity due to decreased crystallinity by effect of the loss of some interlayer water during the impregnation treatment [25].

Transmission electron microscopy (TEM) allowed the shape and size of the nanoparticles constituting the hydrotalcite and catalyst to be clearly observed (Fig. 3). Hydrotalcites usually consist of hexagonal particles the morphology (shape and size) of which depends on various experimental factors, but especially on the aging treatment used in the synthetic procedure [26]. Fig. 3a is a micrograph of solid HT showing relatively uniform hexagonal particles around 200 nm in size, and Fig. 3b one of the catalyst, HT-Pd(0), clearly showing spherical, highly disperse Pd(0) particles 6–8 nm in size.

Table 1
Mg/Al ratio, content of palladium and specific surface area of the synthesized solids.

Solid	Mg/Al ratio	Pd content (%)	S_{BET} (m^2/g)[a]
HT	2.03	–	78
HT-Pd/II)	2.03	0.6	58
HT-Pd(0)	2.03	0.6	61

[a] Specific surface area.

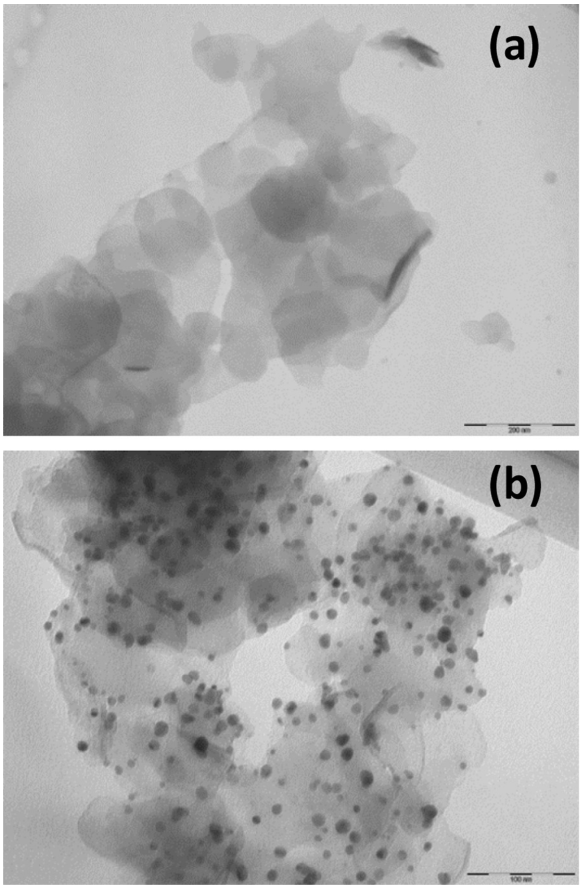


Fig. 3. TEM images of HT (a) and HT-Pd(0) (b).

To obtain information on the oxidation state of palladium after treatment with cyclohexene, X-ray photoelectron spectroscopy (XPS) studies have been performed on the HT-Pd(0) catalyst as well as on the catalyst recovered from the reaction between phenylboronic acid and chlorobenzene. The Pd 3d spectra have been collected and analysed. The binding energy (BE) and full width at half-maxima (FWHM) were analysed and the results obtained is collected in Table 1. For both solids, the spectra show the presence of a main contribution together with a minor component at higher binding energy values. Curve fitting analysis showed that the Pd 3d spectra resulted from two pairs of spin-orbit components. The Pd 3d$_{5/2}$ peak that appears at *ca.* 335 eV can be attributed to Pd(0), in agreement with literature reports [27]. The second signal that appears at *ca.* 327 eV can be assigned to Pd atoms with lower charge density. Semi-quantitative analysis of the XPS signals enabled the Pd(0)/Pd(II) atomic ration to be estimated as 6.9 for the fresh catalyst and 6.2 for the catalyst recovered after Suzuki reaction of phenylboronic acid and chlorobenzene. The Pd(II) species result from residual palladium oxide (PdO) not reduced by cyclohexene.

The presence of PdO in the catalyst was confirmed by using Raman spectroscopy before and after the cyclohexene reduction step. Using a 532 nm laser facilitated sensitive resolution from the electron resonance line for PdO [28]. The main Raman line typical of PdO appears at 620–650 cm^{-1}, the exact position depending on the characteristics of the atmosphere used in the synthetic process. Fig. 4 shows the Raman spectra for HT-Pd(II) and HT-Pd(0). As can be seen, the unreduced catalyst exhibited a strong signal at 639 cm^{-1} corresponding to palladium oxide (Fig. 4a) [29,30] that was considerably decreased by the cyclohexene reductive treatment (Fig. 4b). This confirms the reduction of PdO to metal Pd previously suggested by the XPS measurements.

3.2. Suzuki reaction

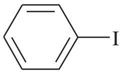
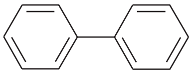
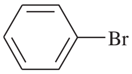
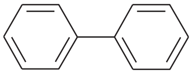
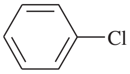
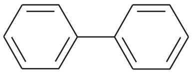
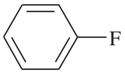
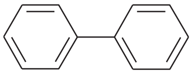
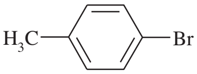
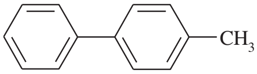
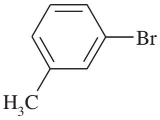
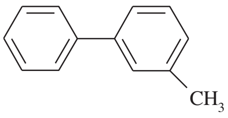
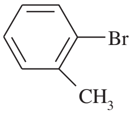
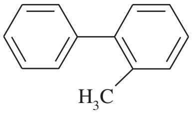
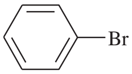
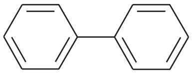
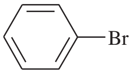
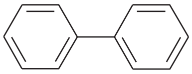
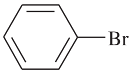
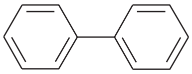
The catalytic activity of the proposed catalyst consisting of Pd nanoparticles supported on hydrotalcite in the Suzuki reaction was assessed by using a temperature of 100 °C and water as solvent throughout. This reaction requires the presence of a base to develop [1]. In previous work with other Pd catalysts [31–33], we found potassium carbonate to be an excellent choice for this purpose. We thus selected it for use in this work as well. In addition, the low water solubility of some reagents was increased by using the surfactant sodium dodecylsulphate.

Table 2 shows the conversion results in the Suzuki reaction of four different halobenzenes with phenylboronic acid (entries 1–4). As can be seen, the catalyst provided excellent results with both iodobenzene and bromobenzene, with near-quantitative conversions within 10 min of reaction. However, the most interesting results were those for chlorobenzene and fluorobenzene. Thus, chlorobenzene exhibited 70% conversion after only 15 min of reaction —an excellent result for a substrate that is rather inactive in the Suzuki reaction. With fluorobenzene, conversion approached 30% after 30 min and was quantitative after 12 h. This result is very interesting since, although fluorinated derivatives have no industrial interest for use in this reaction owing to their high cost, they possess an undeniable academic interest. In fact, there are very few references to the use of fluorobenzene in the Suzuki reaction. Usually, this compound requires the presence of a strongly deactivating group (—NO_2, —CF_3, —$COOCH_3$, —CN or —CHO) [13,34] at position 2 or 4 on the benzene ring in order to trigger the fluorine atom and the oxidative action of palladium, which involves an S_NAr step.

Table 2
XPS data for HT-Pd(0) catalyst and HT-Pd(0) catalyst recovered after reaction between phenylboronic acid and chlorobenzene.

Catalyst	Transition	BE (eV)	FWHM	Pd(0)/Pd(II) ratio
HT-Pd(0)	Pd $3d_{5/2}$	335.0	2.0	6.9
		337.2	1.9	
HT-Pd(0) recovered	Pd $3d_{5/2}$	335.1	2.1	6.4
		337.4	1.9	

Table 3
Suzuki reaction of arylhalides with phenylboronic acid in the presence of HT-Pd(0).[a]

Entry	Arylhalide	Product	Conversion (%)	t_{reac} (min)[b]
1			92	10
2			91	10
3			68	15 (4.5)
4			29	30 (12)
5			82	30 (1.5)
6			76	30 (2.2)
7			72	30 (3.5)
8[c]			90	10
9[d]			88	10
10[e]			88	10

[a] Reaction conditions: $T = 100\,°C$; Phenylboronic acid = 1.5 mmol; Arylhalide = 0.99 mmol; Water (solvent) = 5 mL; K_2CO_3 = 1.98 mmol; Sodium dodecylsulphate = 75 mg; Catalyst = 0.02 mmol Pd.

[b] In brackets the time, in hours, required to achieve conversion values greater than 95%.

[c] First reuse.

[d] Second reuse.

[e] Third reuse.

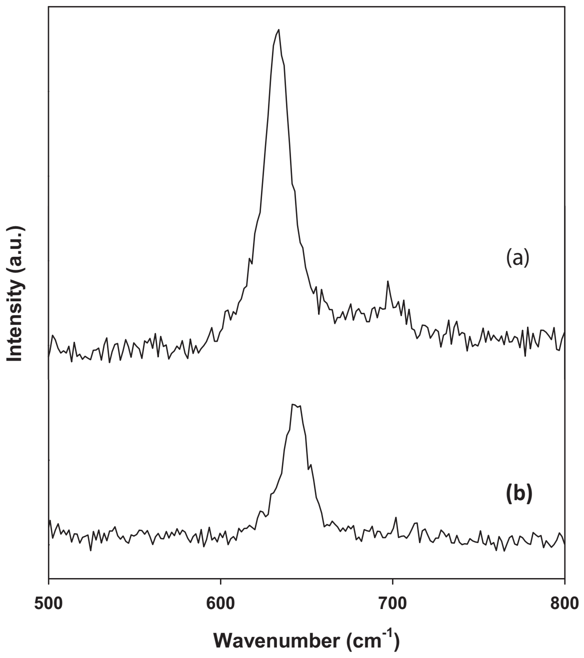


Fig. 4. Raman spectra for HT-Pd(II) (a) and HT-Pd(0) (b) in the 500–700 cm^{-1} region.

One invariable issue in the Suzuki reaction is competition with homocoupling of phenylboronic acid, which also gives biphenyl. In order to rule it out, we conducted two different test series. In one, we examined blank reaction mixtures containing no halobenzene or phenylboronic acid; no biphenyl was detected by gas chromatography after 12 h of reaction. Also, the homocoupling reaction was unequivocally discarded by repeating the process under identical conditions but using 4-, 3- and 2-bromotoluene instead of the halobenzenes as substrates (see entries 5–7 in Table 1). The selectivity to 4-, 3- and 2-methylbiphenyl thus obtained exceeded 99% in all cases, and the amount of biphenyl detected by GC was virtually negligible. Therefore, all biphenyl obtained in the studied reactions was formed by coupling of phenylboronic acid with the halobenzenes.

In using this type of catalyst, one must check whether the catalytic process occurs in a homogeneous or heterogeneous phase. To this end, we performed a hot filtration test, which involves stopping one of the reactions —that of chlorobenzene in our case—at a low conversion level and, while the reaction mixture is still hot, rapidly filtering the catalyst off and replenishing the base in order to allow the reaction to proceed. Monitoring of the reaction under these new conditions revealed a 20% increase in conversion within 20 min. This result is consistent with the presence of palladium in solution and hence with the process partly occurring in a homogeneous phase. This phenomenon was previously observed with catalysts consisting of Pd nanoparticles supported on other materials [11,35,36]. In fact, conversion with the catalyst recovered from the hot filtration test was reduced to 32%. However, because Pd nanoparticles tend to rapidly re-deposit onto the surface of the support, the catalyst should not be reused until all Pd has been allowed to re-deposit. ICP measurements of the liquid mixture of chlorobenzene and phenylboronic acid revealed that the Pd content was only 0.03% 30 min after the reaction was finished and 0.007% 24 h later. As a consequence, waiting for at least 30 min before using the recovered catalyst led to conversion results in the reaction of chlorobenzene with phenylboronic acid similar to those obtained with fresh catalyst (Table 3, entries 8–10).

4. Conclusions

Hydrotalcite-supported palladium nanoparticles readily obtained by impregnation of the support with Pd(II) salt and subsequent reduction to Pd(0) with cyclohexene under very mild conditions provide an excellent catalyst for the Suzuki cross-coupling reaction of aryl halides with phenylboronic acid. Because water is used as solvent throughout, the process develops under environmentally benign conditions. The catalyst is highly active even with strongly inactive substrates such as chlorobenzene and fluorobenzene. The results of tests conducted on substituted chlorobenzenes and blank reaction mixtures suggest that no homocoupling reaction occurs. Also, the results of the hot filtration test indicate that the catalyst operates in both the heterogeneous and homogeneous phase (i.e., that some Pd nanoparticles are leached from the catalyst to the solution). However, cooling the reaction mass causes fast deposition of nanoparticles onto the hydrotalcite support, thereby allowing the catalyst to be efficiently reused.

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