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Palladium and copper supported on mixed oxides derived from hydrotalcite as reusable solid catalysts for the Sonogashira coupling

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Abstract

Magnesium oxide and mixed aluminium–magnesium oxide derived from layered hydrotalcite were used as supports of copper and palladium in various amounts. These solids were used as heterogeneous and reusable solid catalysts for the Sonogashira coupling of iodobenzene and phenyl acetylene in DMF/water as solvent. The activity of MgO was somewhat higher than that of Mg–Al hydrotalcite. The solid catalysts could be reused, but then a decrease in catalytic activity was observed. On reuse, the layered hydrotalcite structure was reconstituted, but no palladium particles were detectable by TEM. Experiments designed to test potential metal leaching showed that the system was heterogeneous. A three-phase test anchoring a iodophenyl reagent to a silica also confirmed that Sonogashira coupling occurred on the solid mixed-oxide catalyst.

Keywords: Sonogashira cross-coupling reaction; Hydrotalcites as support; Reusable heterogeneous catalysts; Three-phase test; Palladium catalysts

1. Introduction

Sonogashira cross-coupling of aryl halides and terminal alkynes has become one of the most versatile synthetic reactions for obtaining substituted aromatic alkynes [1–6]. The main advantages of this palladium-catalyzed reaction are the mild conditions required and its compatibility with a wide variety of other functional groups, including ketones, esters, amides, and alcohols [4–8]. Most of the Sonogashira reactions are carried out in the homogeneous phase in the presence of stoichiometric amounts of organic or inorganic bases, such as carbonates, acetates, or tertiary amines, using as catalyst a mixture of copper(I) salt and palladium complexes [2,3,9–11]. Common solvents for this C–C bond formation are dimethylformamide/water mixtures, triethylamine, diethylamine, tetrahydrofuran, and even hydrocarbons, such as toluene [2,3,9–11].

A natural tendency in catalysis is to develop suitable heterogeneous catalysts for successful processes performed in the homogeneous phase [8,12–21]. Using solid catalysts has the advantage of allowing easy separation from the reaction mixture, enabling recovery and reuse of catalyst for consecutive runs provided that no deactivation and poisoning have occurred. The development of solid, reusable catalysts for Sonogashira coupling is a timely subject; currently there are only few reports addressing the reusability of heterogeneous palladium catalysts [8,10,22–26].

In the present work, we report the catalytic activity for Sonogashira coupling of a series of magnesium oxide and mixed aluminium–magnesium oxides derived from hydrotalcites containing variable amounts of palladium and copper. We have found that these materials with an appropriate Pd/Cu content can be convenient catalysts for this C–C coupling reaction and that the solids can be reused for consecutive runs with a partial decay in activity.

2. Experimental

2.1. Catalyst preparation

Starting from commercial hydrotalcite in its carbonate form (Alcamizer), the mixed Al/Mg oxide was formed by calcination under nitrogen atmosphere at 550 °C. The resulting amorphous mixed oxide was first impregnated with an aqueous solution of the required amount of copper nitrate in the minimum

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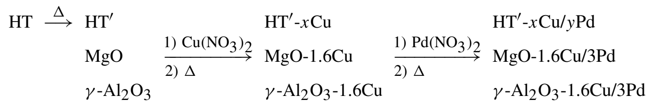


Scheme 1. Diagram of the process for catalyst preparation. HT, layered hydrotalcite; HT′, amorphous mixed oxide; Δ, calcination at 550 °C/N_2 atmosphere; $x = 1.6, 3.6$; $y = 0.2, 3, 5$.

amount of water to produce a wet paste (incipient wetness impregnation). The resulting material was calcined at 550 °C and submitted to consecutive incipient wetness impregnation with the required amount of $Pd(NO_3)_2$ and calcination. An analogous procedure was followed to prepare palladium catalysts using γ-Al_2O_3 and MgO as supports. The process for catalyst preparation is in Scheme 1. The resulting materials containing supported palladium and copper species were characterized by temperature-programmed reduction (TPR); transmission electron microscopy (TEM), using a Philips CM300 FEG system with an operating voltage of 100 kV; X-ray diffraction (XRD), using a Philips X'Pert diffractometer with Cu-K_α radiation and a secondary graphite monochromator; and N_2 absorption, using a Micrometrics ASAP 2000 instrument.

2.2. *Reaction procedure*

Phenyl iodide (2 mmol) and phenylacetylene (2 mmol) were dissolved in a 1 : 1 mixture of water and DMF (5 ml) containing NEt_3 (6 mmol) as a base. The solution was heated to 100 °C in a thermostated silicone oil bath (85 °C measured in the reaction medium), at which point the corresponding palladium supported mixed oxide (142 mg) was added.

At the end of the reaction, the solid catalyst was filtered at reduced pressure. The solid was washed with CH_3CN. The resulting solutions were combined and the solvents removed in a rotavapor apparatus. The residue was weighed, a known amount of nitrobenzene was added as a gas chromatography (GC) internal standard, and the mixture was analysed by GC (Hewlett Packard, 25-m capillary column of cross-linked 5% phenylmethylsilicone) and GC–mass spectroscopy (GC–MS) (using the same column as for GC). Independent runs were stopped at different reaction times to determine the kinetics of the reactions. When the catalyst was reused, the washed solid was added to the solution containing iodobenzene and phenylacetylene following the same experimental procedure and conditions as before. After consecutive reuses, the HT 1.6Cu/0.2Pd, HT 3.6Cu/0.2Pd, and HT 3.6 Cu/3Pd catalysts were characterized by XRD, TEM, and isothermal gas absorption.

2.3. *Three-phase test*

A sample of 4-iodobenzamide covalently bound to silica was obtained by reacting in toluene at reflux temperature a suspension of commercial aminopropyl-functionalized silica (Aldrich) and 4-iodobenzoyl chloride in the presence of a few drops of pyridine. 4-Ethynylphenylene bound to silica was prepared also starting with 4-aminopropyl functionalized silica (1 g) that was reacted with 4-ethynylbenzaldehyde (0.2 g) in toluene (15 ml) at reflux temperature for 6 h. The solid turned orange, indicating formation of the Shiff base. Both silica-functionalized solids were found to be stable under the reaction conditions in the absence of palladium catalyst, and the corresponding organic compounds or its derivatives arising from hydrolysis could be isolated after blank controls. The resulting silica-bound 4-iodobenzamide or 4-ethynylbenzaldehyde were reacted with phenylacetylene and iodobenzene under conditions analogous to those outlined in the previous section. At the end of the reaction, the solids (catalyst and functionalized silica) were collected, washed, and submitted to digestion at reflux temperature with an aqueous 0.5 M solution of NaOH for 2 h (for 4-iodophenyl) or with 2 M HCl in EtOH/H_2O (2 : 1) for 2 days (for 4-ethynylphenyl). After this time, the solution was separated, and the solids were washed with acetonitrile. The combined liquid solutions were concentrated under reduced pressure and analysed by GC. The formation of benzoic acid (for 4-iodophenyl) and ethyl 4-ethylbenzoate and 4-ethenylbenzoate (for 4-ethynylphenyl) was determined by GC–MS.

Table 1
Analytical data and surface area of the palladium supported catalysts used on this work

Catalyst	Cu (wt%)	Pd (wt%)	Surface area (m^2/g)
HT 1.6Cu/3Pd	1.6	3	–
HT 1.6Cu/5Pd	1.6	5	–
HT 3.6Cu/0.2Pd	3.6	0.2	200
HT 3.6Cu/3Pd	3.6	3	198
HT 3.6Cu/5Pd	3.6	5	–
MgO 1.6Cu/3Pd	1.6	3	240
Al_2O_3 1.6Cu/3Pd	1.6	3	120–190

3. Results and discussion

Hydrotalcites and magnesium oxide have been widely used in catalysis as solid bases as well as inorganic supports for transition metals [27–37]. The use of hydrotalcites and magnesium oxide as supports is especially interesting in those processes carried out under basic conditions, because magnesium oxide and hydrotalcites themselves can act as bases [28,31,34,36,38–40]. In our case, catalysts were prepared starting from a magnesium–aluminium hydrotalcite in the carbonate form and proceeding to the stepwise addition of copper and palladium salts in variable amounts. For comparison, we have also considered the corresponding single oxides magnesia and alumina.

After each step of impregnation with the copper and palladium salts, the solid was calcined. The calcination step produces the destruction of the layered structure of the original hydrotalcite, giving rise to amorphous mixed oxides. Calcination and the solid restructuring during thermal treatment have been proven crucial in obtaining a favourable interaction between palladium–copper and the support. The list of the actual hydrotalcite-derived catalysts and their corresponding analytical and textural data are contained in Table 1. The table indicates that all of the solids used had similar surface areas (~200 m^2/g).

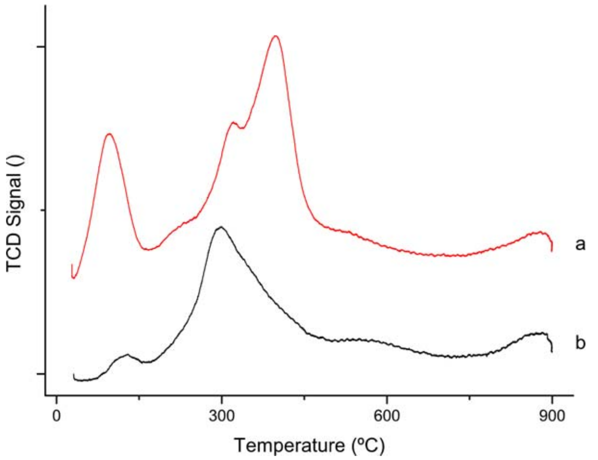


Fig. 1. Thermoprogrammed reduction program (TPR) of samples: (a) HT 3.6Cu/3Pd and (b) HT 3.6Cu/0.2Pd.

When preparing these materials, we limited the amount of palladium to a maximum of 5 wt%, because higher loadings likely would result in the agglomeration of palladium with formation of large, catalytically inactive particles. To study the influence of the relative copper content, we adjusted the percentage of copper to have copper/palladium ratios in the range of 1–30.

Even though the catalytically active oxidation states of both palladium and copper may differ from those of the corresponding nitrates used in the material preparation, we assumed that after some period of induction, catalytically active species with an adequate oxidation state would be formed. To support this hypothesis, we performed TPR of some of our samples using hydrogen as a reductant gas to determine the reducibility of the supported transition metal. Fig. 1a shows hydrogen uptake as a function of heating temperature for a representative palladium-containing sample in which four peaks at 100, 230, 320, and 400 °C were observed. Based on control samples containing exclusively palladium, the peaks at 100 and 400 °C were assigned to the reduction of palladium (II) to palladium (0) in two different environments. The most reducible fraction of palladium (II) (reduction peak at 100 °C) likely corresponds to solvated Pd^{2+} weakly interacting with the mixed oxide support. Meanwhile, the second-most abundant palladium population corresponds to palladium atoms in the oxide form bound to the support. In addition, two other hydrogen uptake peaks with maxima at 230 and 320 °C should correspond to the reduction of copper (II) to either copper (I) or copper (0). To give some support to this assignment, Fig. 1b shows a second TPR profile corresponding to the sample HT 3.6Cu/0.2Pd, in which the minimum amount of palladium is present and the peaks attributed to palladium are almost absent and those corresponding to copper are merged in a single broad peak with the maximum at an intermediate temperature (290 °C). In principle, this would support the assumption that the reduction peaks at 230–320 °C are due to the reduction of CuO formed during calcination of the Cu and Pd supported on the hydrotalcites.

Scanning electron microscopy (SEM) images of the hydrotalcite-derived catalysts indicate that these catalysts consist of large particles (about 50 μm) with some planes and sharp edges, along with a large amount of smaller particles. This morphology is common for all of the hydrotalcite-derived catalysts, which is not surprising considering the common origin of these samples from a single initial hydrotalcite support. Selected images are shown in Fig. 2.

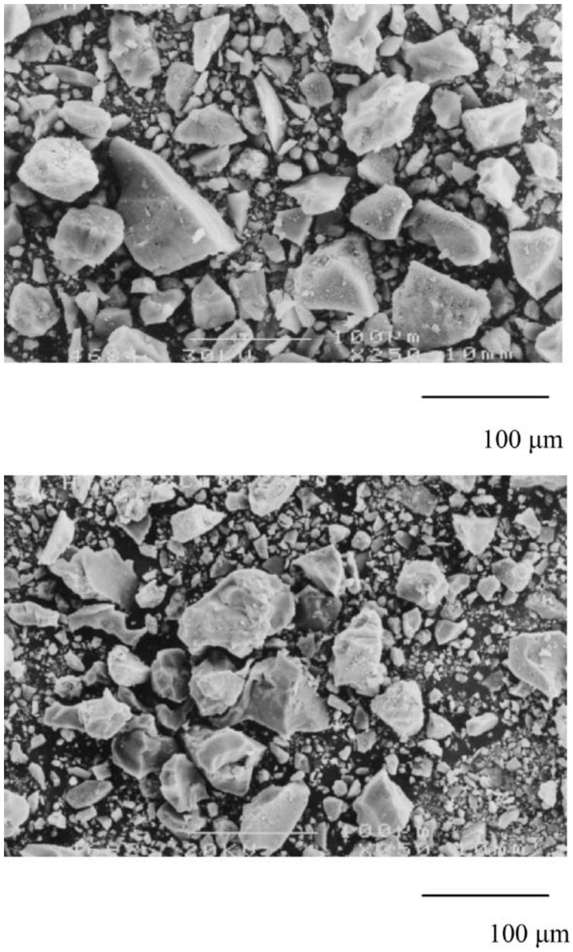


Fig. 2. Scanning electron microscope images of HT 3.6Cu/3Pd (top) and HT 3.6Cu/0.2Pd (bottom) showing the morphology of the HT particles.

TEM was used to determine the crystallite size of palladium particles. The TEM images show the absence of palladium metal particles larger than 20 nm (Fig. 3). Based on this finding, we can conclude that our catalysts most probably contain palladium crystallites or mixed Cu–Pd crystallites smaller than 20 nm.

3.1. Catalytic tests

As a Sonogashira model reaction, we selected the coupling of phenylacetylene and iodobenzene in mixtures of dimethylformamide/water as the solvent and triethylamine as the base. To compare the performance of the different palladium-supported catalysts, we maintained a constant substrate-to-catalyst weight ratio. This means that, depending on the palladium loading, the substrate-to-palladium molar ratio varied from one run to another. We prefer to keep the total weight of the solid catalyst constant, because any variation in the amount

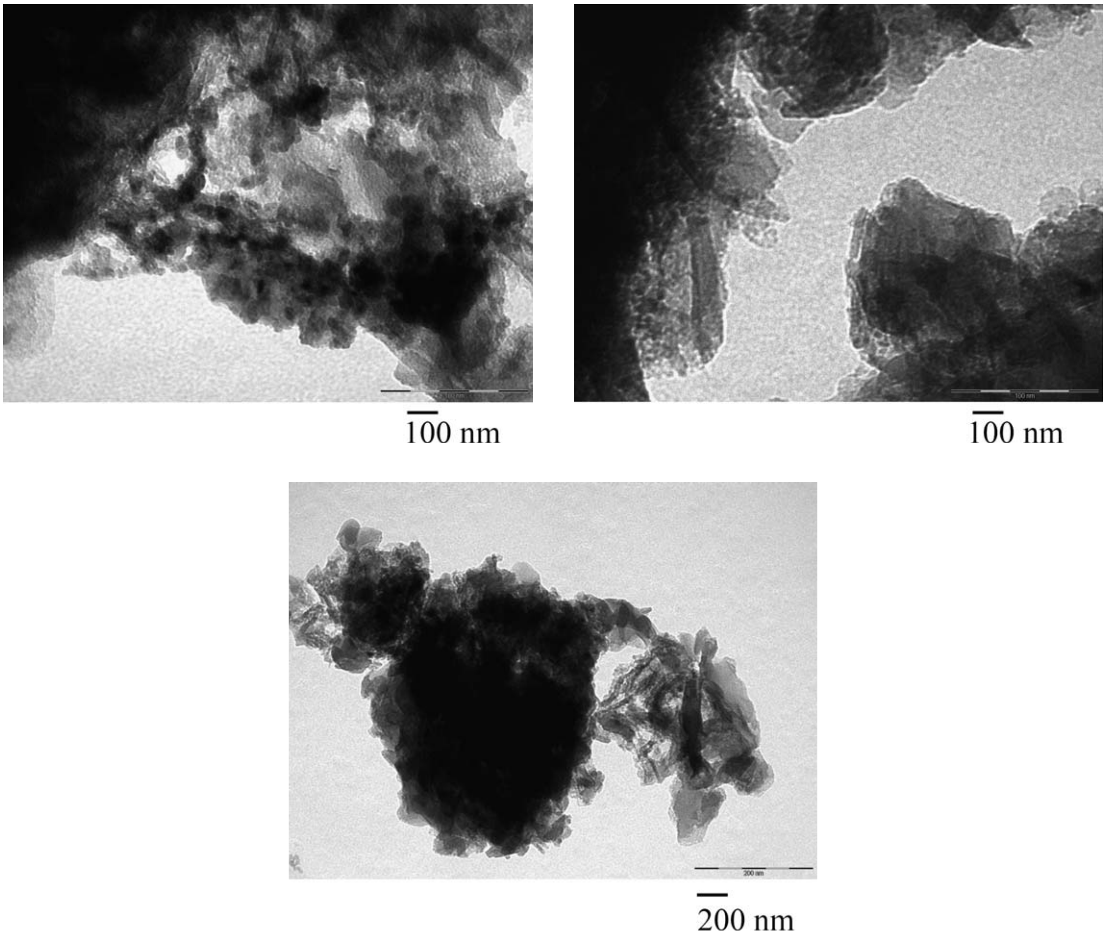


Fig. 3. Transmission electron microscopy (TEM) images of the hydrotalcite derived palladium catalysts.

of catalyst present during the reaction also modifies reagent and triethylamine adsorption, a parameter that we purposely wanted to keep constant during the study.

The only reaction product observed was 1,2-diphenylacetylene, which corresponds to the expected product for Sonogashira coupling. The yields obtained at different reaction times and temperatures are summarized in Table 2. As expected in view of the relative reactivity of the arylbromides compared with aryliodides, yields of Sonogashira coupling products using palladium-supported catalyst and 4-bromoacetophenone as the reagent were considerably lower (<5%) than those obtained with iodobenzene at 6 h.

The reaction product was stable under the reaction conditions, as can be deduced by the fact that no decrease in the yield of diphenylacetylene was observed after disappearance of the reagents and prolonged reaction time (see Table 2, entries 5 and 7).

Blank controls using calcined hydrotalcite, with or without copper, as the catalyst in the absence of palladium (Table 2, runs 1 and 2) showed no activity for Sonogashira coupling. In contrast, palladium supported on calcined hydrotalcite in the absence of copper showed significant activity, although less than that for the analogous sample containing both palladium and copper metals (compare runs 3 and 4 in Table 2). The data in Table 2 seem to indicate that there is an optimum palladium and copper content for the catalyst. Clearly, an increase of more than one order of magnitude in the palladium content is not reflected linearly in the catalytic activity of the solid (Table 2, entries 4, 5, and 9). In contrast, when turnover numbers

Table 2

Results obtained for the Sonogashira coupling of phenylacetylene (2 mmol) and iodobenzene (2 mmol) using palladium containing mixed oxide (142 mg) in DMF/H_2O 1/1 (5 ml) containing NEt3 (6 mmol) as base at 100 °C

Entry	Catalyst	Yield (%)			TON[a]
		30 min	2 h	6 h	
1	HT	0	0	0	0
2	HT 1.6Cu	0	0	0	0
3	HT 3Pd	–	–	68	30
4	HT 1.6Cu/3Pd	65	79	90	27
5	HT 1.6Cu/5Pd	19	100	100	5
6	HT 3.6Cu/0.2Pd	0	5	5	0
7	HT 3.6Cu/3Pd	89	89	89	39
8	HT 3.6Cu/5Pd	19	32	69	4
9	HT 1.6Cu/0.2Pd[b]	36	42	75	247
10	HT 3.6Cu/3Pd[b]	41	72	97	18
11	MgO 1.6Cu/3Pd	70	80	90	32
12	MgO 1.6Cu/3Pd[c]	5	–	21	9
13	Al_2O_3 1.6Cu/3Pd	–	–	39	19

[a] Calculated from the yields at 30 min reaction time.

[b] At 50 °C.

[c] Without base.

are considered, it can be seen that lower palladium loadings gave higher turnover numbers, with high palladium content being detrimental to the intrinsic activity of the palladium atoms (Table 2, runs 4, 5, and 9). We performed a reaction with HT 1.6Cu/5Pd using the same substrate-to-palladium ratio (rather than the same substrate-to-catalyst weight ratio as given in Table 2) as for HT 1.6 Cu/3Pd and observed the same effect as indicated in Table 2—that is, high palladium loading on the mixed oxide was not reflected in a linear increase in catalyst activity. A compromise between high turnover number and high product yield was obtained for the mixed oxides containing 3 wt% of palladium, although it may be that other loadings between 3 and 0.2 wt% could give even higher activity per palladium atom. With regard to the copper, it is also evident that for the two loadings studied, the catalyst containing the lower copper content was the more active. (Table 2, runs 5 and 8). Based on previous literature reports, a possible explanation for the unfavourable effect of high copper loading may be the partial coverage of the palladium nanoparticles by copper metal, leading to reduced catalytic activity.

We addressed the role of the support on the catalytic activity of palladium by studying the catalytic activity of palladium supported on γ-alumina or magnesia under similar conditions. For the palladium supported on γ-alumina, the yields of the Sonogashira coupling product at 6 h of reaction time was considerably lower than those obtained with an analogous catalyst using hydrotalcite-derived mixed oxide as the support (Table 2, entries 4 and 13). In contrast, using magnesia as the support gave activity similar to that of calcined hydrotalcites (Table 2, entries 4 and 11).

According to these results, it is tempting to conclude that basic oxides are more suitable supports for the palladium-catalyzed Sonogashira coupling than neutral supports. This conclusion is certainly not unreasonable, because the presence of bases is required for Sonogashira coupling to proceed. To test whether the basicity of the support can promote the reaction, we performed a control in which triethylamine (which is normally present in stoichiometric amounts in the reactions) was not added to the reaction mixture. Under these conditions, in the absence of added base, the phenylacetylene yield was significantly decreased, although still significant (15%). In addition, palladium supported on magnesia in the absence of extrinsic base showed residual activity (9%). These results indicate that although the basicity of the support has a positive effect, this is not sufficient to avoid the need for extrinsic base.

Most of the reactions were performed at 100 °C. As would be expected, when the temperature was decreased, the reaction slowed. However, at long reaction times the final yields and turnover numbers were similar at both temperatures, indicating that the sole effect of the reaction temperature was on the kinetic energy of the reagents and that it had no influence on catalyst selectivity.

3.2. Metal leaching

When using palladium-supported solids as heterogeneous catalysts, one issue that must be addressed is metal leaching from the solid to the solution, along with the variable contribution of homogeneous-phase catalysis. To determine whether the reaction using palladium-containing mixed oxides actually occurs through a heterogeneous catalytic process, we performed two types of experiments. The simplest of these experiments involved performing twin reactions in the presence of the solid catalyst until a conversion of 50% was reached, at which point the solid catalyst was removed in one of the reactions by filtering the solids with a preheated syringe while hot and then washing the solids with hot solvent. After filtration of the solids, the clear solution containing the filtrate and the washings was allowed to react further in the absence of solids. Comparing the yields of the Sonogashira products in the two twin reactions with and without solid catalyst established that filtration of the solids stopped the reaction. This suggests that no leaching of palladium occurred during the reaction. In contrast, the twin reaction carried out under the same conditions proceeded further, reaching 75% of final conversion. The time-conversion plot in Fig. 4 shows the results of removing solids from the reaction mixture.

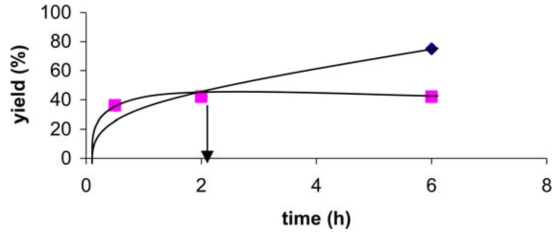
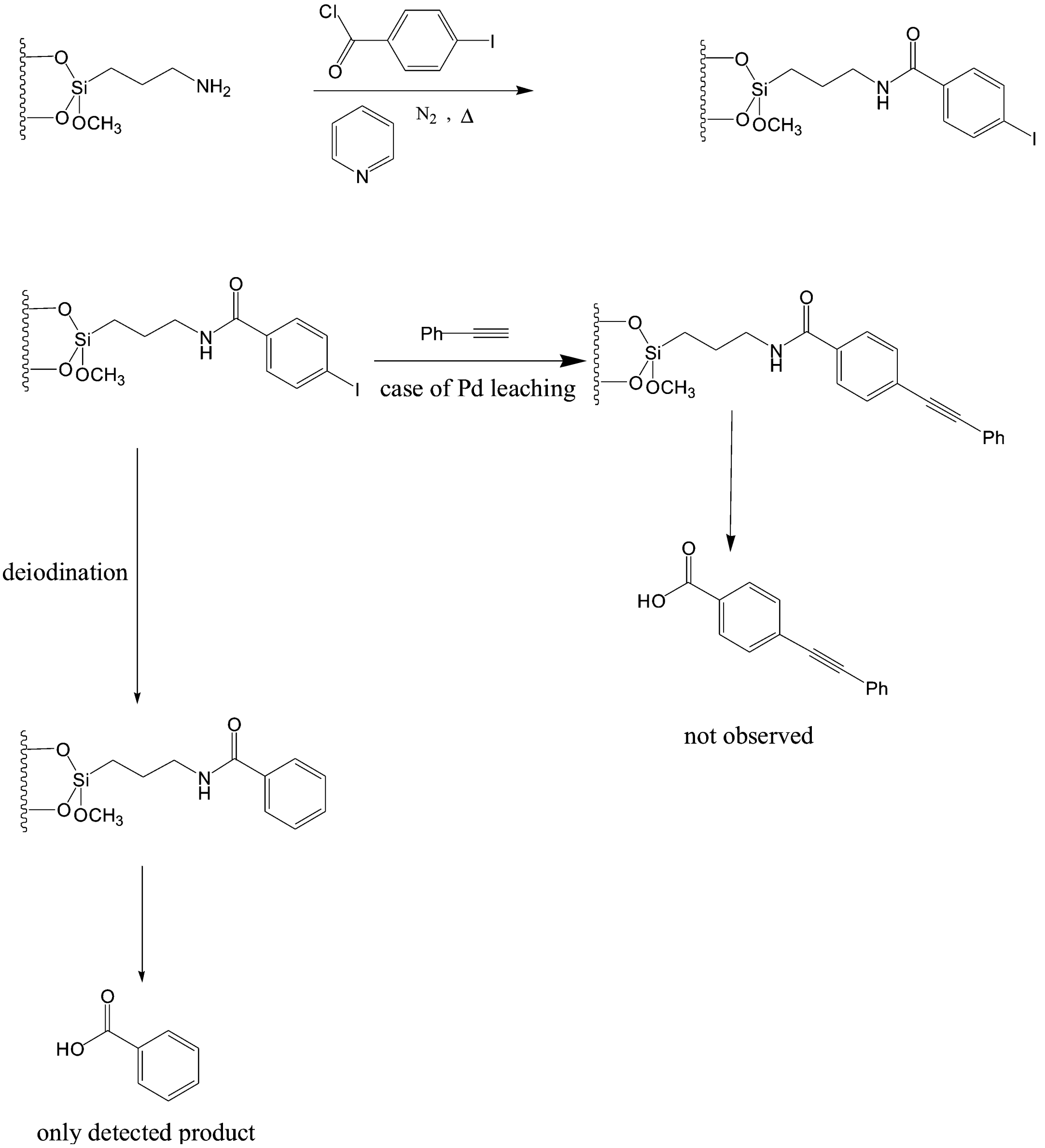


Fig. 4. Time conversion plot for the Sonogashira reaction of iodobenzene (2 mmol) and phenylacetylene (2 mmol) in dimethylformamide/H_2O 1/1 (5 ml) at 100 °C: (◆) in the presence of palladium containing mixed oxide as catalyst (142 mg); (■) initiating the reaction as before in the presence of palladium containing mixed oxide (142 mg) and filtrating the solid in hot at the time indicated in the arrow and allowing the clear solution to continue the reaction.

Leaching control based on filtration of the solids while the mixture is still hot has been questioned for palladium catalysts. It has been shown that colloidal palladium particles present in solution can reprecipitate onto the solid support during filtration due to the inevitable decrease in temperature during the workup [41,42]. The term “boomerang catalyst” has been coined to describe this phenomenon, indicating that palladium species leached into the solution can be easily readsorbed onto the support on cooling.

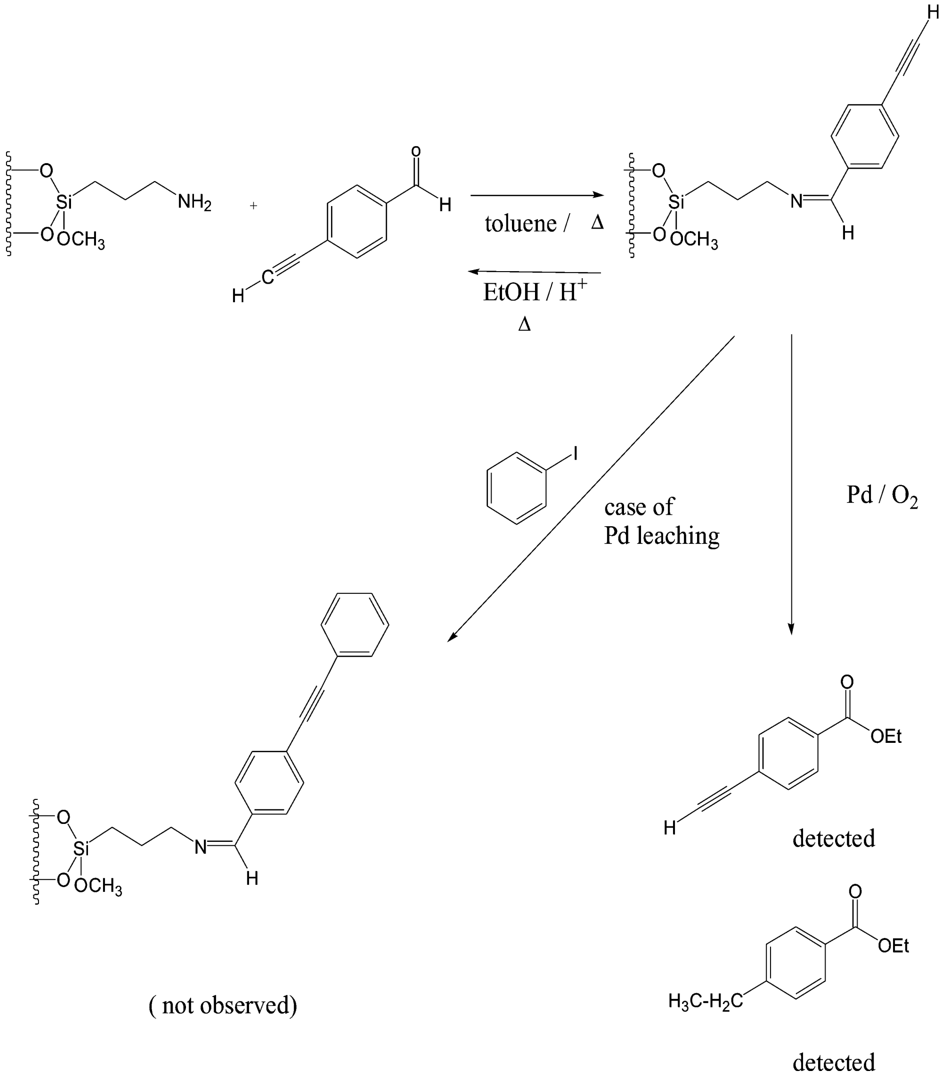
To firmly disregard or support the occurrence of such a “boomerang”-like process in our study, we also performed two three-phase tests as described previously [41–43]. In these three-phase tests, an aryl halide or an aryl acetylene analogous to these used as the Sonogashira reagents in solution were covalently anchored to a metal-free solid support, such as silica, and these solids were present during a reaction carried out under typical conditions in the presence of the solid catalysts. After the reaction occurred in the liquid phase, the solids were surveyed for the presence of the intact reagents or for their transformation into covalently anchored Sonogashira products. Schemes 2 and 3 summarize the preparation of the two func-



Scheme 2. Diagram of the preparation of the iodophenyl-functionalized silica and the different stages of the three phase test of palladium leaching anchoring a iodophenyl derivative.

tionalized silicas containing covalently anchored a iodophenyl or 4-ethynylphenyl moieties, as well as the different stages of the three-phase tests.

Controls performed independently using the iodophenyl-functionalized and 4-ethynylphenyl silicas were used to optimise the hydrolysis conditions for the maximum recovery of the anchored iodophenyl- or 4-ethynylphenyl-derived products and to determine the best analytical techniques for detecting the reagents and reaction products. In addition to the palladium-supported catalyst (HT 1.6Cu/3Pd) and the silica containing either 4-iodophenyl or 4-ethynylphenyl, we added dimethylformamide/water solvent, the base, and the two reagents of Sonogashira coupling. Thus, the presence of Sonogashira coupling in the solution (arising from the reaction of iodophenyl and phenylacetylene in the liquid phase) provides evidence that catalytically active palladium species (in either the homogenous or heterogeneous phase) were present in the medium. Moreover, if some of the reagents (either phenyl iodide or phenylacetylene) or the product contributed to the solubility of palladium species in the solution, then they also would be present during the test to aid in the solubilization of palladium. For instance, Davis and co-workers detected soluble Pd(II) species arising from the oxidative addition of aryl halide to palladium metal [41,42]. Using the three-phase test, we were able to confirm that coupling of phenylacetylene with the anchored iodobenzamide (Scheme 2) or anchored 4-ethynylphenyl (Scheme 3) did not occur, and consequently we can conclude that the Sonogashira product was actually promoted heterogeneously by the solid catalyst. It is interesting to note that in the three-phase experiment of 4-iodophenyl anchored to silica, the only product detected was benzoic acid, indicating that dehalogenation of iodobenzoic acid occurred, whereas for the anchored 4-ethynyl-



Scheme 3. Diagram of the preparation of the 4-ethynylphenylene-functionalized silica and the different stages of the three phase test of palladium leaching.

benzaldehyde, C≡C triple-bond hydrogenation together with aldehyde oxidation products were found.

To further check whether some palladium had leached from the solid, chemical analysis of palladium in the liquid-phase reaction mixture was carried out after filtration of the solid while hot and concentration of the solution. No palladium was detected in the reaction mixture (detection limit, 0.1 ppm).

3.3. Catalyst reuse

Another important issue concerning the use of a solid catalyst is its reusability and stability under reaction conditions. This issue is particularly relevant considering that some reports have described the recycling of palladium catalysts [2–4, 9,11,12,24]. To gain insight into this issue, we performed three consecutive uses of the three hydrotalcite-supported palladium catalysts after filtration and washing with CH_3CN; the results are shown in Fig. 5. As could have been anticipated, catalytic activity decreased on reuse of the catalyst, although the solids remained active for the three uses. This deactivation was observed in the second run for HT 1.6Cu/5Pd and in the third run for HT 1.6Cu/3Pd and HT 3.6Cu/3Pd.

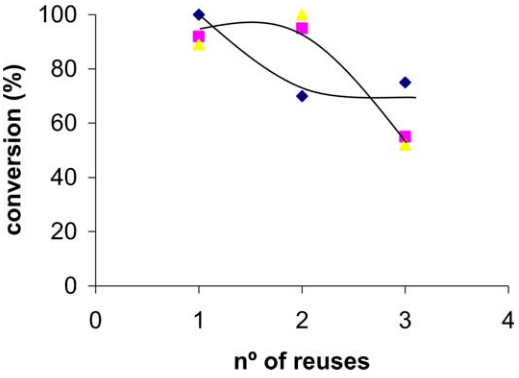


Fig. 5. Influence of the number of uses on the catalytic activity for the Sonogashira coupling of PhI (2 mmol) + phenylacetylene (2 mmol) at 100 °C in DMF/H_2O after 6 h reaction time. (▲) HT 3.6Cu/3Pd; (■) HT 1.6 Cu/5Pd; (◆) HT 1.6Cu/3Pd.

To understand the origin of deactivation, we studied the structural changes in the hydrotalcite-derived HT 1.6 Cu/5 Pd catalyst after three consecutive recycles using XRD, TEM, and surface area measurements. Of particular interest was determining whether or not larger palladium particles were formed on the hydrotalcite support during the repeated uses. Agglomeration of palladium is a common phenomenon, linked to the reaction temperature and the presence of water in the reaction medium. XRD of hydrotalcite HT 1.6Cu/5Pd after three uses exhibited weak peaks at 2θ 12, 24, 35, 37, 61, 66° that were compatible with regeneration of the original hydrotalcite-layered structure from the amorphous mixed oxide. It is known that mixed oxides originating from hydrotalcite calcination tend to restore the layered hydrotalcite structure on hydration [44,45]. This phenomenon has been termed the "hydrotalcite memory effect," indicating that the amorphous mixed oxides derived from hydrotalcite maintain a preorganization that can finally lead to a profound restructuring into hydrotalcites [45]. This transformation of the mixed oxides during the Sonogashira reaction in aqueous media indicated by XRD is also reflected in the TEM images of the used catalyst samples. Fig. 6 shows selected TEM images in which the typical layered structure of hydrotalcite can be clearly seen. It is noteworthy that no palladium nanoparticles are apparent in the TEM images, ruling out the occurrence of extensive palladium agglomeration, which is one of the main causes of deactivation of palladium-supported catalysts.

Finally, N_2 absorption indicates the transformation of solid supports from amorphous mixed oxides into hydrotalcite structure, as reflected by the drastic reduction of the solid surface area from about 200 m^2/g for the initial amorphous mixed oxides to <10 m^2/g. According to the catalytic data, the recovery of this layered structure does not play a detrimental role in catalytic activity in proportion to the large reduction. This is most likely due to the fact that under the reaction conditions using DMF/H_2O as the solvent, the substrate and reagents can access to the intergallery space, whereas gas absorption of dry samples does not measure the interlamellar surface. To determine whether or not regeneration of a partially deactivated catalyst can be achieved by restoring the amorphous structure, we calcined a sample of HT 1.6Cu/5Pd after it was used three times as a catalyst. Using HT 1.6Cu/5Pd as a catalyst had restored the typical layered structure of hydrotalcite, and we wanted to convert the sample into the amorphous mixed oxide structure characteristic of the fresh catalyst. However, catalytic testing with three-times-used HT 1.6Cu/5Pd after calcination showed somewhat lower activity (70%) than that for the fresh catalyst and similar to that for HT 1.6Cu/5Pd reconstituted with a lay-

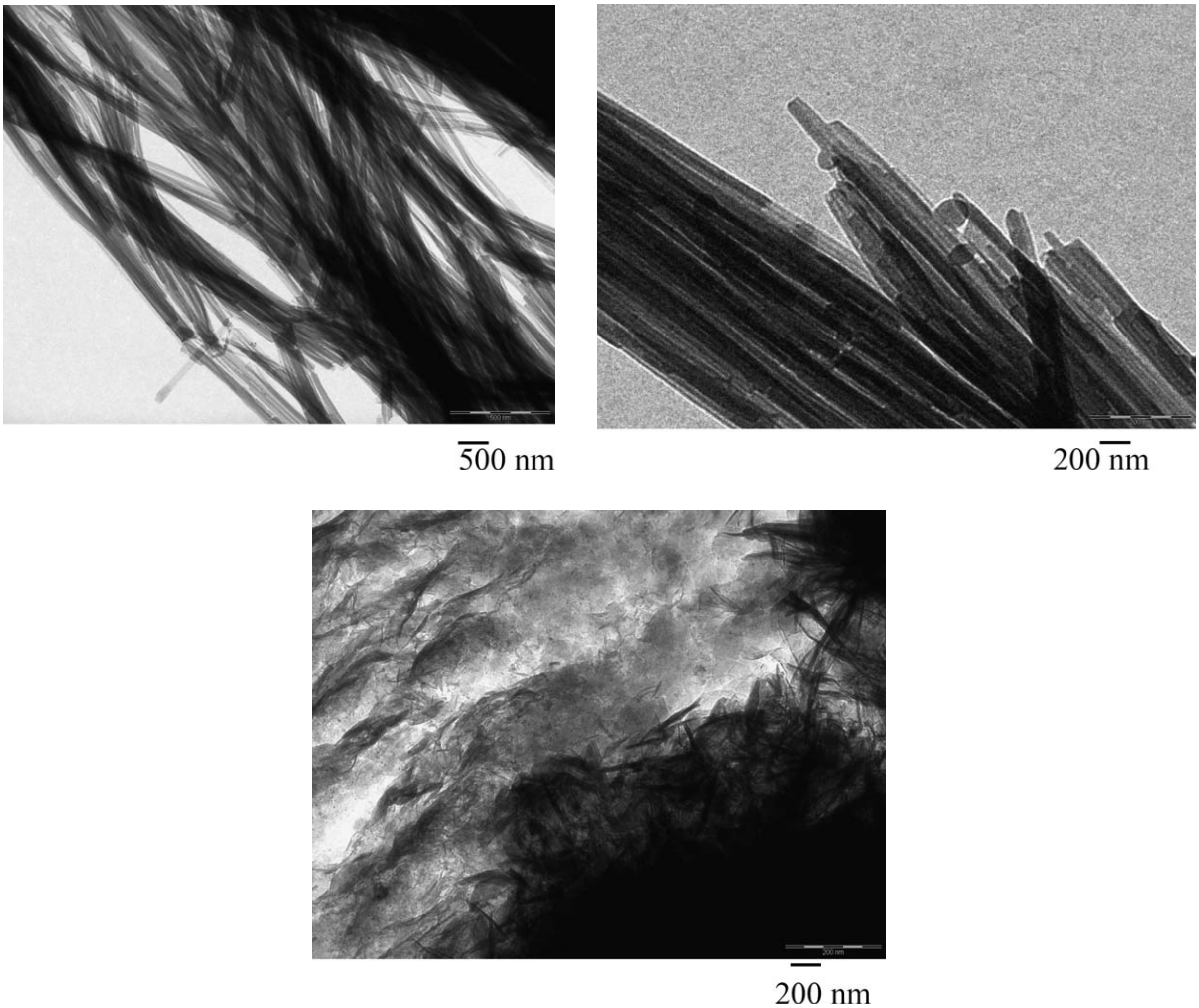


Fig. 6. Transmission electron microscopy (TEM) images of the hydrotalcite derived catalysts after being used for the Sonogashira coupling.

ered structure. Thus, calcinations (at least at the temperature at which it was done here) is not a suitable reactivation procedure. Nevertheless, it must be noted that our hydrotalcite-supported palladium catalyst still exhibited high activity on reuse, and that there was a paucity of reusable catalysts for Sonogashira coupling.

4. Conclusion

Pd and Cu supported on hydrotalcites have been shown to be highly active and selective catalysts for the Sonogashira reaction of aryl iodides and phenylacetylene in aqueous media. The presence of copper enhanced the activity of the palladium support, but copper-free palladium support also exhibited residual activity. An optimum palladium-to-copper atomic ratio was found for low palladium content. The catalyst is truly heterogeneous and reusable. Although some restructuring of the mixed oxides formed by calcination of the initial hydrotalcite occurred, recovering the hydrotalcite layer structure, the catalysts retained a significant part of their activity. Palladium was most likely in the form of nanoparticles of <20 nm diameter that did not agglomerate during catalyst use and recycling. Given the current interest in reusable palladium nanoparticles and the scarcity of reusable solid catalysts for Sonogashira reactions, the palladium-supported catalyst presented here is a step forward in the development of highly active, heterogeneous, and reusable Sonogashira catalysts.

Acknowledgments

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