

Palladium supported on hydrotalcite as a catalyst for the Suzuki cross-coupling reaction

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Abstract—The efficiency of various palladium salts as catalysts in the Suzuki cross-coupling reaction, and the influence of the base and temperature used on its conversion, were studied. The use of PdCl₂ supported on hydrotalcite as catalyst in the presence of potassium carbonate as base was found to provide the best results. Reaction temperatures above 90 °C ensured conversion levels on a par with those for many homogeneous catalysts.

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1. Introduction

The palladium-catalysed Suzuki cross-coupling reaction has for some time been one of the most powerful tools for the formation of carbon–carbon bonds in organic synthesis.^{1–3} In most cases, the reaction involves a homogeneous palladium catalyst and a ligand of variable nature such as a phosphine.^{2,4–6} Recently, however, some cross-coupling processes have used palladium supported on various types of supports such as sepiolites,^{7,8} silica,⁹ zeolites and zeolitic materials,^{10–12} layered double hydroxides,^{13,14} carbon^{15,16} and organic complexes bound to inorganic solids.^{17–21} These heterogeneous catalysts are being increasingly used to circumvent some shortcomings of homogeneous catalysts such as the need to remove the catalyst after the reaction, its poor reusability and potential environmental pollution problems. Also, palladium ligands and precursors are expensive, which severely restricts their industrial use.

Hydrotalcite is a naturally occurring mineral of the layered double hydroxide family that constitutes a major class of anionic clay materials. Hydrotalcite is structurally related to brucite [Mg(OH)₂]: magnesium cations are at the centres of octahedra the vertices of which are occupied by hydroxyl groups to form stacks. In hydrotalcite, some Mg²⁺ ions are replaced by aluminium cations, which introduces a charge deficiency in the layers. In order to ensure electroneutrality in the overall structure, the positive charge is countered by

carbonate ions present in a disorderly manner in the interlayer spacing, which also contains crystallization water (Fig. 1).²² Hydrotalcite has been extensively used by our research group in organic processes such as the epoxidation of limonene,^{23,24} the Meerwein–Ponndorf–Verley reduction^{25–27} and the α -arylation of diethyl malonate.²⁸

In this work, we prepared various catalysts consisting of Pd²⁺ supported on hydrotalcite by using various precursor salts and employed them in the Suzuki cross-coupling reaction in the presence of various inorganic bases (see Scheme 1). We studied the influence of the aryl halide and temperature used. All catalysts and the hydrotalcite

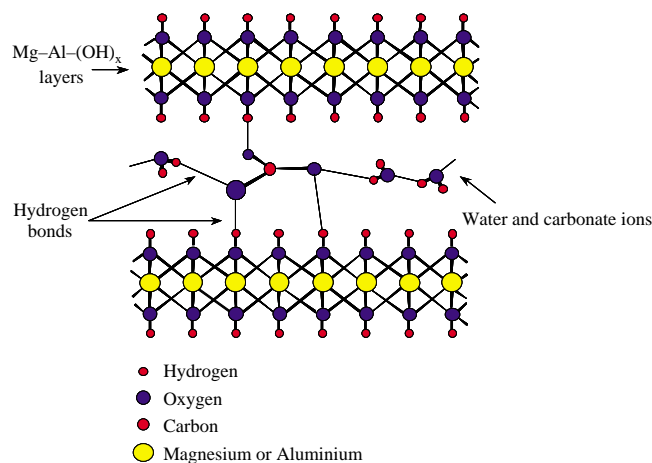
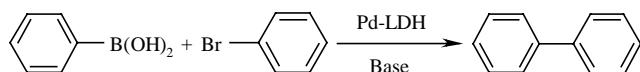


Figure 1. Structure of hydrotalcite.

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Scheme 1. Suzuki cross-coupling reaction studied.

precursor were characterized in terms of structure and surface properties by using various instrumental techniques.

2. Results and discussion

2.1. Characterization of catalysts

Based on the elemental analysis, the hydrotalcite and the palladium catalysts that were supported on it had an Mg/Al ratio of 2:1 and a Pd²⁺ content of 1%.

The XRD analysis of solid HT (Fig. 2) revealed a high crystallinity. As can be seen from the XRD pattern, the solid had a typical structure of stacked layers similar to those previously found by Reichle et al.²⁹ in hydrotalcites. Therefore, using the hydrotalcite as a support for our Pd catalysts caused no structural change in the mineral as the catalysts deposited on its outer surface only (XRD patterns for the catalysts not shown). Some anions from the palladium salt may have been exchanged with the carbonate ions in the interlayer spacing. Such an exchange would have altered the interlayer distance, which is defined by the lattice parameter *c* (viz. three times the distance between two adjacent layers). Based on the position of the strongest line, corresponding to the crystallographic indices (003), the lattice distance, *d*₀₀₃, was calculated and used to determine *c* (*c* = 3 · *d*₀₀₃, Table 1). The *c* values thus obtained differed, which suggests that some carbonate ions were replaced by the anions of the palladium salt; however, the difference was so small that it had no practical consequences—particularly in catalytic terms.

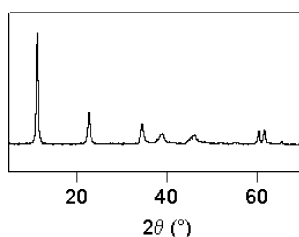


Figure 2. XRD patterns for HT.

Table 1. Specific surface area and lattice parameter *c* for the catalysts

Catalyst	<i>c</i> (Å) ^a	<i>S</i> _{BET} (m ² /g) ^b
HT	23.1844	75.7
HT–PdCl ₂	23.1075	86.5
HT–Pd(AcO) ₂	23.2647	86.2
HT–PdCl ₄	23.2227	87.3

^a Lattice parameter.

^b Specific surface area.

Table 1 also shows the specific surface area of the hydrotalcite and catalysts. As can be seen, it increased slightly upon deposition of the metal.

2.2. Suzuki reaction

The Suzuki cross-coupling reaction is known to require a base in order to abstract the proton during the reductive elimination of the organopalladium intermediate leading to the end-product.¹ The bases most frequently used in this process are carbonates or acetates of alkaline metals such as sodium or potassium, as well as some organic amines. The best choice in each case must be determined on an individual basis. To this end, we used our hydrotalcite-supported Pd catalysts in the Suzuki reaction between phenylboronic acid and bromobenzene in the presence of various inorganic bases. The sole reaction product obtained in all cases was biphenyl.

Table 2 shows the conversion results and Figure 3 the temporal variation of the conversion for the three studied catalysts in the presence of K₂CO₃ as the base. All reactions exhibited a linear relationship between the natural logarithm of the bromobenzene concentration and the reaction time, which suggests that the reaction is first-order in such a concentration:

$$\ln(c_0/c) = kt$$

where *c*₀ and *c* are the bromobenzene concentrations at times zero and *t*, respectively, *k* the rate constant and *t* time.

Table 2. Conversion obtained in the Suzuki cross-coupling reaction^a

Catalyst	Base	Conversion (%) ^b	<i>k</i> (h ^{−1}) ^c
HT–PdCl ₂	K ₂ CO ₃	47.2	0.312
	Rb ₂ CO ₃	2.1	0.003
	CsF	2.2	0.003
	K ₃ PO ₄	7.1	0.009
HT–Pd(AcO) ₂	K ₂ CO ₃	27.21	0.171
	Rb ₂ CO ₃	1.3	0.004
	CsF	2.5	0.005
	K ₃ PO ₄	10.64	0.047
HT–PdCl ₄	K ₂ CO ₃	25.6	0.137
	Rb ₂ CO ₃	3.9	0.006
	CsF	1.0	0.003
	K ₃ PO ₄	8.24	0.024
Blank-1 ^d	K ₂ CO ₃	0	—
Blank-2 ^e	—	0	—

^a Reactions conditions: 1.98 mmol PhBr; 3 mmol PhB(OH)₂; 3.96 mmol K₂CO₃; 0.24 g (0.04 mol%); 5 mL toluene, *T* = 55 °C.

^b Conversion to biphenyl (reaction time: 3 h).

^c Rate constant.

^d Blank without catalyst.

^e Blank without base.

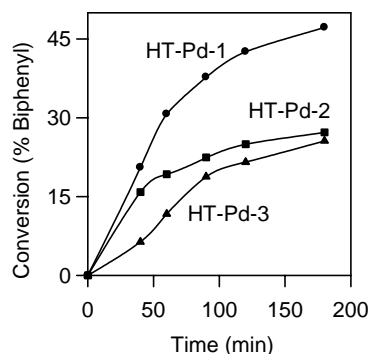


Figure 3. Temporal variation of the biphenyl conversion in the Suzuki cross-coupling reaction.

As can be seen from Table 2, K_2CO_3 was the base providing the best conversion and catalytic activity results, well ahead of K_3PO_4 . The other bases studied exhibited very poor conversion. Also, catalyst $PdCl_2$, in the presence of K_2CO_3 , was that providing the best results; it was therefore adopted for further testing, which included examining the influence of the reaction temperature and aryl halide, as well as catalyst leaching and reuse tests.

The influence of temperature on the conversion and rate of the Suzuki reaction between bromobenzene and phenylboronic acid using catalyst $Pd-HT-1$ in the presence of K_2CO_3 was examined at 55, 75, 90 and 110 °C. Table 3 shows the biphenyl conversion and rate constant obtained as described above. As expected, raising the temperature substantially increased the conversion, which exceeded 90% after only 3 h of reaction at 90 °C. These results are quite good; in fact, they are as good as or even better than those obtained with other heterogeneous catalysts and many homogeneous ones. The activation energy for the process as calculated from an Arrhenius plot was 47 kJ/mol.

Table 3. Conversion obtained in the Suzuki cross-coupling reaction at a variable temperature^a

T (°C)	Conversion (%) ^b	k (h^{-1}) ^c
55	47.2	0.312
75	72.4	1.795
90	90.6	2.873
110	95.3	4.168

^a Reactions conditions: 1.98 mmol PhBr; 3 mmol PhB(OH)₂; 3.96 mmol K_2CO_3 ; 0.24 g HT-Pd-1 (0.04 mol%); 5 mL toluene.

^b Conversion to biphenyl (reaction time: 3 h).

^c Rate constant.

We then studied the influence of the phenyl halide on the coupling reaction, using the previous catalyst ($HT-PdCl_2$) and base (K_2CO_3). One of the major shortcomings of this process is its inefficiency with aryl chlorides or fluorides as substrates. This has aroused much interest in developing efficient catalysts (particularly aryl chlorides, which are more readily available and inexpensive than aryl bromides). Most catalysts for the Suzuki reaction are of the homogeneous type, and not all provide acceptable conversion.^{4,30–33} We used both chlorobenzene and fluorobenzene and found the reaction to develop as summarized in Table 4. As can be seen, chlorobenzene provided good results: the conversion amounted to 28% after only 3 h of reaction at quite a low temperature (55 °C). Fluorobenzene gave poorer, but still promising, results; in fact, aryl fluorides

Table 4. Influence of the phenyl halide used in the Suzuki cross-coupling reaction^a

Phenylhalide	Conversion (%) ^b	k (h^{-1}) ^c
Ph-F	14.9	0.090
Ph-Cl	28.1	0.191
Ph-Br	47.2	0.312

^a Reactions conditions: 1.98 mmol PhX; 3 mmol PhB(OH)₂; 3.96 mmol K_2CO_3 ; 0.24 g HT-Pd-1 (0.04 mol%); 5 mL toluene, $T=55$ °C.

^b Conversion to biphenyl (reaction time: 3 h).

^c Rate constant.

started to be used in this process only 2 years ago^{34,35} as the C–F bond is the strongest of all C–halogen bonds and its cleavage had been achieved in only a few cases and never with heterogeneous palladium catalysts.

The heterogeneous character of the Pd^{2+} catalyst was determined in a leaching test on the reaction between bromobenzene and phenylboronic acid at 55 °C using solid $HT-PdCl_2$ as the catalyst and K_2CO_3 as the base. After 30 min, the reaction was stopped—the biphenyl conversion at the time was 23.1%—to remove the catalyst and base by filtration. The remaining solution was supplied with K_2CO_3 and the reaction allowed to proceed at 55 °C for a further 24 h. The biphenyl conversion thus obtained was identical, so the catalytic action of Pd^{2+} was of the heterogeneous type. Also, we have made experiments without bromobenzene, and the conversion to biphenyl is negligible, so we rule out the homocoupling of the boronic acid.

Finally, we studied the reusability of the catalyst, again by using the reaction between bromobenzene and phenylboronic acid at 55 °C in the presence of $HT-PdCl_2$ as the catalyst and K_2CO_3 as the base. Figure 4 shows the results obtained after three catalytic cycles; as can be clearly seen, the catalyst lost some activity after each reuse. Therefore, reusing the catalyst entails its prior reactivation. This is also the case with other heterogeneous catalysts used in the Suzuki reaction.

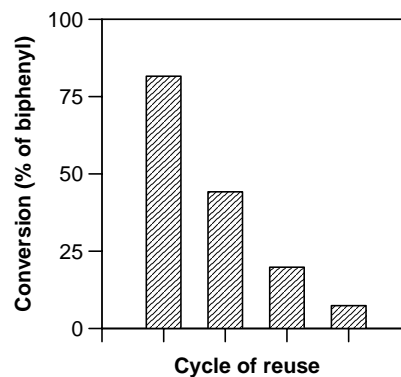


Figure 4. Influence of catalyst reuse on the biphenyl conversion in the Suzuki cross-coupling reaction.

3. Conclusions

The results obtained in this work show that the deposition of palladium salts on hydrotalcite is an effective method for preparing solids that are active catalysts in the Suzuki cross-coupling reaction—particularly those obtained by depositing $PdCl_2$. The biphenyl conversion in the reaction between bromobenzene and phenylboronic acid was found to depend on the particular base used, of which K_2CO_3 proved the best among those tested. These catalysts are also active in the reduction of chloro- and fluorobenzenes, where few catalysts—particularly of the heterogeneous type—are effective. The temperature is one other crucial variable here. The activation energy for the process was calculated to

be 47 kJ/mol. Finally, testing revealed the catalytic process to be completely heterogeneous in nature.

4. Experimental

The hydrotalcite used was prepared by mixing two solutions of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 2:1 ratio, using a coprecipitation method described elsewhere.³⁶ In a typical synthetic run, a solution containing 0.3 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.15 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 250 mL of de-ionized water was used. The solution was slowly dropped over 500 mL of an Na_2CO_3 solution at pH 10 at 60 °C under vigorous stirring. During precipitation, the pH was kept constant by adding appropriate volumes of 1 M NaOH. The suspension obtained was kept at 80 °C for 24 h, after which it was filtered and washed with 2 L of de-ionized water. Any residual nitrate ions in the hydrotalcite structure were removed by exchange with carbonate ions. For this purpose, 2.5 g of the LDH was dispersed in 125 mL of de-ionized water, the dispersion being supplied with 250 mg of Na_2CO_3 and refluxed for 2 h. Then, the solid was separated by centrifugation and the water discarded. The hydrotalcite obtained following exchange with carbonate ions was designated HT.

The hydrotalcite was used as a support for the palladium catalysts, which were obtained by impregnation, a method previously used by our group to prepare Pd catalysts supported on various materials such as silica and aluminium orthophosphate.^{37,38} The catalysts used in this work were obtained as follows: the amounts of PdCl_2 , $\text{Pd}(\text{AcO})_2$ and Na_2PdCl_4 required to obtain a final Pd content of 1% in the catalyst were dissolved in *N,N*-dimethylformamide and supplied with 2 g of hydrotalcite in a flask. The mixture was kept at room temperature in a rotavapor for 24 h, after which the solvent was evaporated at a low pressure to obtain the three supported palladium catalysts, which were designated HT– PdCl_2 , HT– $\text{Pd}(\text{AcO})_2$ and HT– PdCl_4 according to whether they were obtained from the chloride, acetate or tetrachloropalladate, respectively, as precursor.

The catalysts and the hydrotalcite support were characterized by using various instrumental techniques including X-ray diffraction and nitrogen adsorption.

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