

# Suzuki cross-coupling reactions over Pd(II)-hydrotalcite catalysts in water

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## Abstract

We studied the Suzuki cross-coupling reaction between bromobenzene and phenylboronic acid at room temperature in aqueous media containing  $K_2CO_3$  as the base and solids consisting of Pd(II) supported on an Mg/Al hydrotalcite as catalysts. Based on the results, a surfactant facilitating the dissolution of phenylboronic acid in water is required for the reaction to develop at room temperature. Sodium dodecylsulphate proved the most effective surfactant among those tested for this purpose, which included anionic, cationic and neutral compounds. The conversion and selectivity results were excellent and on a par with previously reported values. However, ICP-MS measurements of palladium content before and after the reaction revealed that some metal in the catalyst was dissolved, so the catalytic process was not completely heterogeneous; rather, the reaction involves substantial homogeneous catalysis.

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**Keywords:** Suzuki cross-coupling; Palladium; Hydrotalcite; Water; Surfactant

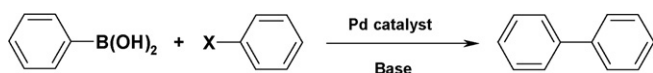
## 1. Introduction

The Suzuki cross-coupling reaction, which involves the formation of biphenyl by coupling of an aryl halide or triflate to a phenylboronic acid in the presence of a palladium catalyst (see Scheme 1), constitutes one of the most widely used methods for the formation of carbon–carbon bonds in organic synthesis [1–5]. In most cases, the reaction is conducted with homogeneous catalysts, which are effective even with inactivated substrates [6] and provide excellent turnover values; also, the reaction medium is most often an organic solvent. However, removing residual palladium and its ligands from the reaction medium is usually a labour-intensive process [7], which has restricted the industrial use of these catalysts; also, the organic solvents employed can be the source of environmental problems. In addition, the high cost of palladium ligands and the difficulty of removing the catalyst from the reaction mass for reuse have further restricted the use of homogeneous catalysts on a large scale. The previous

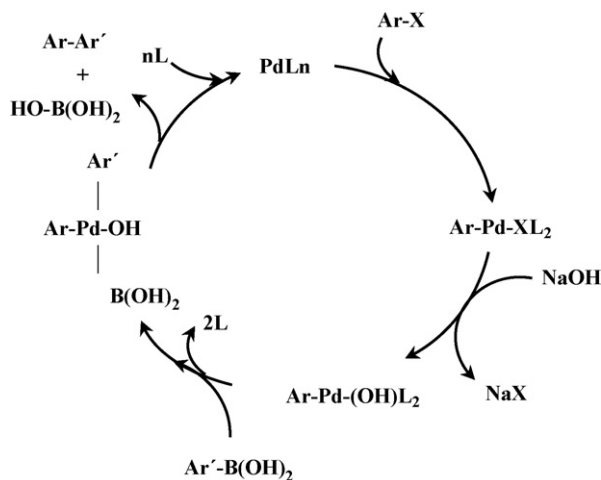
problems can in principle be minimized by using heterogeneous catalysts, which are usually more inexpensive, readily obtained and easily removed from the reaction medium (*e.g.* by filtration) than are homogeneous catalysts. However, few heterogeneous catalysts can compete in activity with homogeneous catalysts for the Suzuki cross-coupling reaction; specially effective among the former are palladium ligands supported on, or bound to, inorganic solids [8–12], Pd(0) and Pd(II) salts deposited on various supports [13–16]. Although the Suzuki cross-coupling reaction has scarcely been conducted with heterogeneous Pd catalysts and water as solvent, an increasing number of applications have been reported in recent years [17–20].

Based on its generally accepted mechanism (Scheme 2) [1], the Suzuki reaction requires the presence of a base to develop to an adequate extent. In previous work, we reported the synthesis of catalysts consisting of palladium ligands and salts [12,16,21], and their use in the cross coupling of arylbenzenes with phenylboronic acid in the presence of various bases. The results showed  $K_2CO_3$  to be the most effective base and toluene the best solvent: no leaching was observed at a reaction temperature of 55 °C. In this work, we conducted the reaction under more environmentally benign conditions; to such an end, we used the same

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Scheme 1. General Suzuki cross-coupling reaction.



Scheme 2. Generally accepted mechanism for the Suzuki reaction in a homogeneous phase.

catalysts as in previous work, but room temperature and water rather than toluene as solvent.

Hydrotalcites have aroused much interest by virtue of their potential uses in various scientific fields such as organic synthesis [22–24]. The structure of these compounds is based on that of a natural mineral called hydrotalcite [25]. This is a magnesium–aluminium hydroxyl-carbonate of formula  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  structurally similar to brucite,  $\text{Mg}(\text{OH})_2$ , except for the fact that some  $\text{Mg}^{2+}$  ions have been replaced with  $\text{Al}^{3+}$ , which results in the presence of layers bearing positive charge that is countered by carbonate ions in the interlayer spacing. Replacing the magnesium, aluminium or both cations with another metal, or the carbonate with another anion, allows a large family of compounds known as hydrotalcite-like compounds (HTs) or layered double hydroxides (LDHs) to be prepared.

## 2. Experimental

### 2.1. General procedure for the preparation of Mg/Al hydrotalcite

Hydrotalcite (HT) was prepared from 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 an Mg(II)/Al(III) ratio of 2, using a coprecipitation method described elsewhere [25]. In a typical synthetic run, a solution containing 0.2 mol of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.1 mol of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 250 mL of de-ionized water was used. This solution was slowly dropped over 500 mL of an  $\text{Na}_2\text{CO}_3$  solution at pH 10 at 60 °C under vigorous stirring, the pH being kept constant by adding appropriate volumes of a 1 M solution of NaOH during precipitation. The suspension thus obtained was kept at 80 °C for 24 h, after which the solid was filtered off and washed with 2 L of de-ionized water.

The resulting HT was ion-exchanged with carbonate to remove intercalated ions between layers. The procedure involved suspending the solid in a solution containing 0.345 g of  $\text{Na}_2\text{CO}_3$  in 50 mL of bidistilled, de-ionized water per gram of HT at 100 °C for 2 h. Then, the solid was filtered off *in vacuo* and washed with 200 mL of bidistilled, de-ionized water. The HT thus obtained was subjected to a second ion-exchange operation under the same conditions. The final solid was characterized from its X-ray diffraction pattern, which exhibited the typical signals for hydrotalcite [26], and by elemental analysis, which provided the empirical formula  $\text{Mg}_{0.70}\text{Al}_{0.35}(\text{OH})_2(\text{CO}_3)_{0.225} \cdot 0.72\text{H}_2\text{O}$ .

### 2.2. General procedure for synthesizing the catalysts

The HT solid was used to support the  $\text{Pd}(\text{CH}_3\text{COO})_2\text{Py}_2$  complex by mixing appropriate amounts of palladium acetate, pyridine and HT at 80 °C for 1 h, after which the solid was filtered off and washed with 100 mL of toluene. The catalyst thus obtained was named HT-Pd(AcO<sub>2</sub>)Py<sub>2</sub>. The other catalysts were synthesized by impregnation, intercalation or precipitation as described elsewhere [26].

### 2.3. Suzuki cross-coupling reaction

The Suzuki cross-coupling reaction was conducted in a two-mouth flask containing appropriate amounts of boronic acid, phenyl bromide and  $\text{K}_2\text{CO}_3$  in addition to 5 mL of water, 0.02 mmol of Pd and 75 mg of surfactant, at room temperature. One of the flask mouths was fitted with a reflux condenser and the other was used for sampling at regular intervals. The reaction mass was stirred throughout the process. The resulting products were identified from their retention times by GC–MS analysis.

## 3. Results and discussion

### 3.1. Preliminary tests

One of the primary aims of modern chemical industry is the avoidance or reduction of the use of environmentally undesirable reactants. As noted in the Introduction, one way of reducing the environmental impact of industrial processes is by replacing polluting organic solvents with more benign alternatives or even water if at all possible. Massive energy consumption is one other serious problem with many industrial processes. In this work, we conducted the Suzuki reaction by using room temperature and water as solvent. The final working conditions were established by performing preliminary tests involving various solvents and temperatures. In previous work, we found 55 °C and toluene containing  $\text{K}_2\text{CO}_3$  to be the optimum choice for the Suzuki cross-coupling reaction of phenylboronic acid not only with bromobenzene [12], but also with fluorobenzene [21], both of which occurred with no palladium leaching. The preliminary tests in this work were performed in different solvents at room temperature. Table 1 shows the conversion to biphenyl in the reaction between bromobenzene and phenylboronic acid

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