

## **MODIFIED BINH THUAN BENTONITE AS AN EFFICIENT AND RECYCLABLE CATALYST FOR THE SUZUKI REACTION BETWEEN IODOBENZENE AND PHENYLBORONIC ACID**

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### **SUMMARY**

*Modified Binh Thuan bentonite catalyst was prepared by exchanging with aqueous solution of PdCl<sub>2</sub>, affording a catalyst loading of 0.14 mmol of Pd/g (ICP-MS). The Pd<sup>2+</sup>-exchanged bentonite catalyst was assessed for its activity in the the Suzuki cross-coupling reaction between iodobenzene and phenylboronic acid to form biphenyl as the principal product. The reaction was performed using 0.2 mol% catalyst at 100°C in dimethylformamide (DMF) and in the presence of K<sub>3</sub>PO<sub>4</sub> as a base, with biphenyl being formed in a conversion of up to over 95% (GC) without added phosphine ligands. It was also observed that the modified bentonite catalyst could be facilely separated from the reaction mixture by centrifugation or simple filtration, and could be reused in subsequent reactions without significant degradation in activity.*

### **I - INTRODUCTION**

Transition metal-catalyzed cross-coupling reactions have attracted interests over the past thirty years in organic synthesis, in particular as convenient techniques for the formation of carbon-carbon bonds [1]. Numerous reactions have been developed to achieve cross-coupling, of which the Suzuki reaction is one of the most efficient methods for the synthesis of biaryl derivatives [2]. These biaryl units have exhibited practical applications in the production of pharmaceuticals, herbicides, as well as engineering materials such as conducting polymers and liquid crystals [3]. Catalysts used in the standard Suzuki processes are generally based on homogeneous palladium phosphine complexes, which are rarely recoverable without elaborate and wasteful procedures, and therefore commercially undesirable. Phosphine ligands are expensive, toxic and generally unrecoverable. In large-scale application, the phosphines might be a

more serious economical burden than even the palladium itself [4]. In this context, heterogeneous palladium catalysts have recently emerged as a greener alternative to homogeneous processes so that catalysts can be recovered and reused [5].

Modified Binh Thuan bentonite catalysts have been explored for applications in several organic transformations, especially by Ngo Thi Thuan and co-works. Their works have focused on Fe<sup>3+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>-exchanged bentonites as solid acid catalysts for alkylation, isomerization reactions etc [6]. We recently exchanged Binh Thuan bentonite with Pd<sup>2+</sup> cation and employed this catalyst for the Heck cross-coupling reaction of iodobenzene and styrene to produce stilbene derivatives, and the catalyst could be reused in subsequent reactions without significant degradation in activity [7]. In this paper, we wish to report the application of Pd<sup>2+</sup>-exchanged Binh Thuan bentonite as an efficient and recyclable catalyst for the Suzuki reaction

between iodobenzene and phenylboronic acid to form biphenyl as the principal product, without the use of any phosphine ligand. To our best knowledge, this is the first time the Suzuki reaction using modified Binh Thuan bentonite catalyst has been investigated and reported in Viet Nam.

## II - EXPERIMENT

### 1. Catalyst preparation and characterization

The modified Binh Thuan bentonite catalyst was prepared according to our previous report [7]. Natural bentonite was treated with 10% HCl aqueous solution at 70°C for 6 h to eliminate impurities, washed several times with distilled water until no trace of Cl<sup>-</sup> was observed using AgNO<sub>3</sub> solution as indicator, dried and ground, achieving bentonite-H<sup>+</sup>. The bentonite-H<sup>+</sup> was then exchanged with 0.016 M aqueous solution of PdCl<sub>2</sub> at 70°C for 24 h. The solid was filtered off under vacuum, washed several times with distilled water until no trace of Cl<sup>-</sup> was observed as indicated by AgNO<sub>3</sub> solution, dried and ground. Particles passing through 100 mesh sieve were then collected, achieving bentonite-Pd<sup>2+</sup> catalyst.

X-ray powder diffraction (XRD) patterns of the bentonite-H<sup>+</sup> were recorded using CuK<sub>α</sub> radiation source on a diffractometer at Institute of Petroleum, Petrovietnam, Ho Chi Minh City. The surface areas of the bentonite-Pd<sup>2+</sup> catalyst were analyzed by BET method according to nitrogen physisorption measurements at 77 °K, and experiments were conducted at Analytical Laboratory, Institute of Chemical Technology at Ho Chi Minh City, Vietnamese Academy of Science and Technology. The palladium loading on the bentonite-Pd<sup>2+</sup> catalyst was determined using inductively coupled plasma - mass spectroscopy (ICP-MS) measurements, and experiments were conducted at Center of Analytical Services and Experimentation, Ho Chi Minh City.

### 2. Catalysis studies

Chemicals were purchased from Sigma-Aldrich and Fisher, and used as received without further purification. Unless otherwise

stated, a mixture of 4-iodobenzene (0.12 ml, 1.08 mmol), phenylboronic acid (0.1976 g, 1.62 mmol), K<sub>3</sub>PO<sub>4</sub> (0.8628 g, 3.24 mmol), and hexadecane (0.12 ml) as the internal standard in dimethylformamide (5 ml) were added to a round-bottom flask containing the required amount of the bentonite-Pd<sup>2+</sup> catalyst. The flask was heated at the required temperature with magnetic stirring. Reaction conversions were monitored by withdrawing aliquots (0.1 ml) from the reaction mixture at different time intervals, and quenching with water. The organic components were extracted into diethylether, dried over Na<sub>2</sub>SO<sub>4</sub> and analyzed by gas chromatography (GC) with reference to hexadecane. Product identity was also further confirmed by gas chromatography — mass spectroscopy (GC-MS).

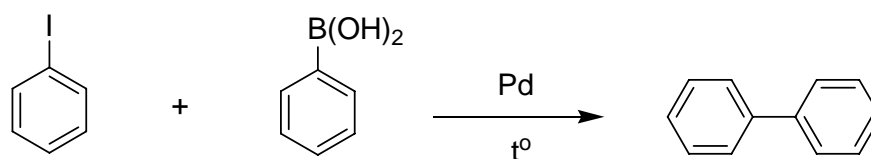
## III - RESULTS AND DISCUSSION

Similar to our previous report where modified Binh Thuan bentonite catalyst was prepared for Friedel-Crafts alkylation reactions [8], XRD patterns of the bentonite-H<sup>+</sup> showed that bentonite treated with 10% HCl aqueous solution essentially contained montmorillonite. It was also observed that calcite impurities were almost eliminated during the course of HCl treatment. Nitrogen physisorption measurements of the bentonite-H<sup>+</sup> and the bentonite-Pd<sup>2+</sup> catalyst reported BET surface areas of 275.94 m<sup>2</sup>/g and 214.28 m<sup>2</sup>/g, respectively. Inductively coupled plasma - mass spectroscopy (ICP-MS) analysis of the bentonite-Pd<sup>2+</sup> catalyst showed a palladium loading of 0.14 mmol/g. The metal loading observed in this research was comparable to that of several other solid-supported palladium catalysts in the literature [9].

The bentonite-Pd<sup>2+</sup> catalyst was assessed for its activity in the Suzuki reaction initially by studying the coupling of iodobenzene with phenylboronic acid to form biphenyl as the principal product (Scheme 1). The sensitivity of a heterogeneously catalyzed reaction to different solvents can usually be of extreme importance, depending on the nature of the catalyst support material [10]. It was therefore decided to investigate the solvent effect in the Suzuki

reaction, using 0.5 mol% of the bentonite-Pd<sup>2+</sup> catalyst at 120 °C in the presence of Na<sub>2</sub>CO<sub>3</sub> as a base. Dimethylformamide (DMF), isoamyl alcohol, and *p*-xylene were adopted as the polar aprotic solvent, polar protic solvent, and nonpolar solvent, respectively. In the literature, a number of solvents such as DMF, toluene, dimethyl glycol, dioxane ect. worked effectively for most of the Suzuki reactions [11]. Experimental results showed that the reaction

carried out in DMF afforded a conversion of 49% after 7 h, while the reaction in isoamyl alcohol and *p*-xylene gave conversions of only approximately 20% under the same conditions, respectively (Figure 1). It was previously hypothesized that DMF might be essential for the reduction of Pd (II) to Pd (0), which was the real active species for the coupling reaction [3]. However, the problem still remains to be solved and needs further investigations.



Scheme 1: The Suzuki reaction between iodobenzene and phenylboronic acid

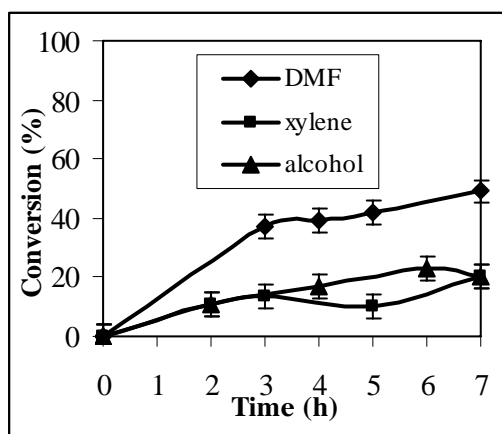


Figure 1: Effect of solvents on reaction conversions

We then decided to investigate the effect of bases on the reaction conversions, using DMF as the solvent at 120 °C in the presence of 0.5 mol% of the bentonite-Pd<sup>2+</sup> catalyst. It is generally accepted that a base is obviously necessary to accelerate the transmetalation step in the catalytic cycle of the Suzuki reaction [12]. The most commonly used base in the Suzuki reaction is Na<sub>2</sub>CO<sub>3</sub>, but stronger bases such as NaOH, K<sub>3</sub>PO<sub>4</sub> and Ba(OH)<sub>2</sub> were previously reported to give better results in some cases [13]. In this research, however, the Suzuki reaction using Na<sub>2</sub>CO<sub>3</sub> afforded the coupling

product in a significantly lower conversion than reactions using CH<sub>3</sub>COONa and K<sub>3</sub>PO<sub>4</sub> as bases (Figure 2). After 7 h, a conversion of 76% was observed for the case of CH<sub>3</sub>COONa, while the reaction using K<sub>3</sub>PO<sub>4</sub> proceeded with up to 97% conversion being achieved under the same conditions. Styring and co-workers also reported similar effects of bases in the Suzuki reaction, where the combination of DMF as the solvent and K<sub>3</sub>PO<sub>4</sub> as the base exhibited dramatically better conversion than the case of Na<sub>2</sub>CO<sub>3</sub> [14]. Suzuki and co-workers previously reported that K<sub>3</sub>PO<sub>4</sub> worked better than Na<sub>2</sub>CO<sub>3</sub> for the case of sterically hindered reagents in homogeneous Suzuki reactions [15]. Although iodobenzene and phenylboronic acid used in this research are not sterically hindered, the similar effects of bases might originate from the nature of the bentonite-Pd<sup>2+</sup> catalyst. However, further exploration is necessary to elucidate the problem.

With these results in mind, we therefore studied the effect of catalyst concentration on reaction conversions, using DMF as the solvent and K<sub>3</sub>PO<sub>4</sub> as the base at 120 °C. As with previous reports, the higher the catalyst concentration was used, the higher the reaction rate was observed. Almost quantitative conversion of iodobenzene to biphenyl was achieved within 2 h at the palladium

concentration of 0.8 mol% relative to iodobenzene. Decreasing the catalyst concentration resulted in a drop in reaction rate, with 97% and more than 96% conversions were obtained after 7 h at palladium concentrations of 0.5 mol% and 0.2 mol% respectively (Figure 3). The reaction using 0.1 mol% catalyst proceeded with slower rate, with a conversion of 94% being achieved after 7 h. The catalyst concentrations used in this study were comparable to those of several previous reports covering different aspects of the Suzuki reaction, where the palladium concentrations varied from less than 0.1 mol% to more than 1 mol%, depending on the nature of the catalysts as well as the substrates [12].

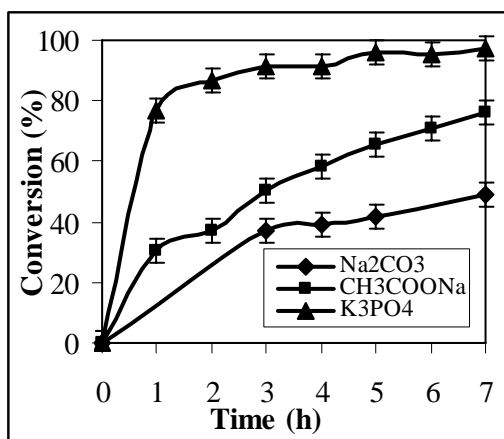


Figure 2: Effect on bases on reaction conversions

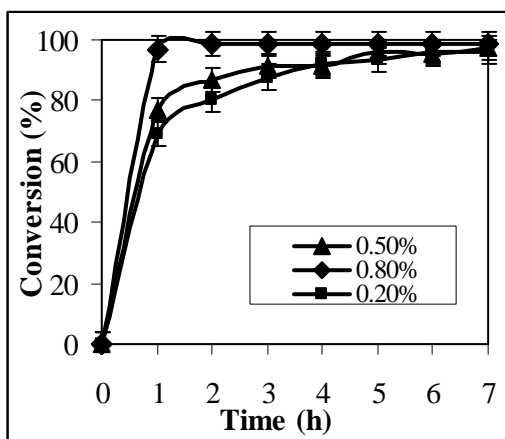


Figure 3: Effect of catalyst concentration on reaction conversions

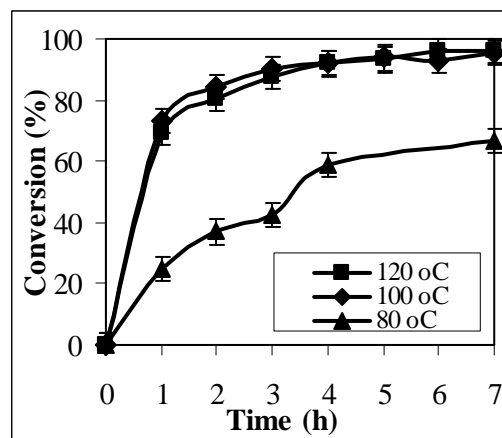


Figure 4: Effect of temperature on reaction conversions

The effect of the reaction temperature was then investigated varying from 80°C to 120°C, using 0.2 mol% catalyst in DMF, and in the presence of K<sub>3</sub>PO<sub>4</sub> as the base. It was decided to use 0.2 mol% instead of 0.5 mol% of the bentonite-Pd<sup>2+</sup> catalyst for the reaction as the difference in reaction rates was not considerable. Experimental results showed that, within experimental errors, the reaction rate remained almost identical when increasing reaction temperature from 100°C to 120°C. Increasing reaction temperature to above 100°C was therefore unnecessary. As expected, decreasing the reaction temperature from 100°C to 80°C resulted in a significant drop in the conversion of iodobenzene, from 96% to only 66% after 7 h (Figure 4). Indeed, the temperature range of 90°C to 120°C has been the most commonly used for Suzuki transformation using different types of palladium catalysts [5]. The most effective reaction temperature for the Suzuki reaction using the bentonite-Pd<sup>2+</sup> catalyst in this research was therefore in good agreement with the literature.

An important point concerning the use of a heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical applications of the palladium-catalyzed Suzuki reaction. In the best case the catalyst can be recovered and reused before it eventually deactivates completely. At the same time, the

catalyst recovery can also reduce the environmental pollution caused by heavy metals used in the catalyst system [16, 17]. The bentonite-Pd<sup>2+</sup> catalyst was therefore investigated for recoverability and reusability. After the reaction, the catalyst was separated from the reaction mixture by centrifugation, washed several times with toluene, DMF, water and ethanol to remove any physisorbed reagents. The recovered catalyst was then dried and reused in further reaction under identical condition to the first run. Experimental results showed that the bentonite-Pd<sup>2+</sup> catalyst could be reused in further reaction without significant degradation in activity (Figure 5). A conversion of approximately 90% was still achieved after 7 h for the second run. Although it was previously reported that almost no loss of activity was observed for reused palladium catalysts for the Suzuki reaction in some cases, no kinetic data was provided, and only conversions at the end of the experiment were mentioned [18]. Unfortunately, stable activity can not be proven by reporting only similar reaction conversions at long times. Kinetic studies are the true test of catalyst deactivation.

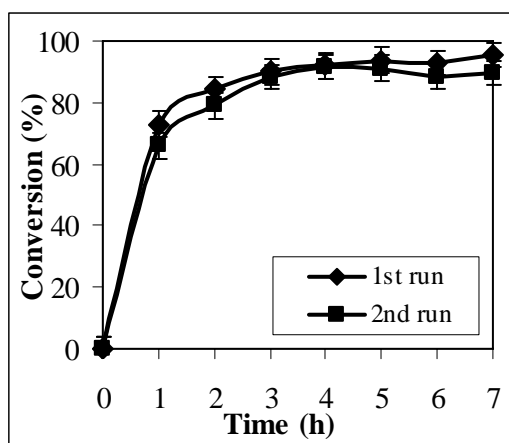


Figure 5: Study of catalyst recycling in the Suzuki reaction

#### IV - CONCLUSIONS

In summary, modified Binh Thuan bentonite catalyst was prepared by the cation exchanging method, using aqueous solution of PdCl<sub>2</sub>. A

palladium loading of 0.14 mmol/g of bentonite catalyst was afforded, determined by ICP — MS. For the first time in Viet Nam, to our best knowledge, the modified bentonite catalyst was used as an efficient heterogeneous catalyst for the Suzuki reaction of iodobenzene with phenylboronic acid to produce biphenyl as the principal product. Using 0.2 mol% catalyst at 100 °C in DMF and in the presence of K<sub>3</sub>PO<sub>4</sub> as a base, the Suzuki reaction proceeded efficiently with biphenyl being formed in a conversion of up to over 95%, determined by GC. It was also observed that the modified bentonite catalyst could be facily separated from the reaction mixture by centrifugation or simple filtration, and could be reused in subsequent reaction without significant degradation in activity. Our results here demonstrated the feasibility of exploring Binh Thuan bentonite as a green material to produce heterogeneous catalysts for the Suzuki reaction as well as other useful transition metal-catalyzed organic transformations.

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