



# The Effect of Bases, Catalyst Loading and Reaction Temperature on the Catalytic Evaluation of Supported Palladium(II) Catalyst in the Mizoroki-Heck

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## Abstract

The coupling reaction between aryl halide of 4-bromoacetophenone with methyl acrylate in the presence of supported palladium(II) catalyst has been investigated. The synthesized catalyst is air and moisture-stable turned out to be efficient and selective for Mizoroki-Heck reaction under operating conditions. Three parameters have been explored to monitor the performance of catalytic activities which focused on the effect of bases, catalyst loading and reaction temperature. Furthermore, the catalyst can be easily recovered quantitatively by simple filtration and reused in at least three consecutive cycles of Mizoroki-Heck reaction.

**Keywords:** Supported Palladium(II) Catalyst, Heterogeneous Catalysis, Mizoroki-Heck Reaction

## 1. Introduction

The most important carbon-carbon bond forming process among palladium catalyzed reaction is the arylation of alkenes also known as Mizoroki-Heck. Recently, attention has been motivated to use supported palladium catalysts in organic transformation [1]. Inspired by the need of green chemistry, heterogeneous catalysts drew great interest for synthetic chemists [2]. Basically, the preparation of supported catalyst depends upon the suitability of the catalyst support to give a proper designed catalyst of high activity, selectivity, stability, recoverability and reusability [3,4]. However, the nature of the solid supports and the type of anchorage must be carefully chosen in order to be resistant towards the solvent as well as reactant attacked. Agrell et al., (2003) reported that several types of solid supports have been studied and used for heterogeneous catalysts are inorganic and organic materials [5]. Metal complexes can be deposited on a solid material such as metal oxides, carbon and polymer through wet or dry impregnation, via deposition-precipitation and deposition-reduction [6]. Among these supports, organic polymers have been widely used, extensively explored and various strategies for the attachment of metal species have been developed. It has been reported in the literature that the use of polystyrene supported palladium(II) catalyst has received tremendous attention in carbon-carbon coupling reaction due to the inert, non-toxic, non-volatile, ease of handling, insoluble and often recyclable [7]. Our previous paper presented the synthesis and characterization studies of polystyrene supported palladium(II) catalyst [8]. Continuing interest in the catalytic activity of polystyrene supported palladium(II) catalyst encouraged us to investigate the Mizoroki-Heck reaction of aryl bromide using the synthesized catalyst. In this paper, we reported the catalytic studies of 4-bromoacetophenone with methyl acrylate using several parameters.

## 2. Materials and Methods

### 2.1 Materials, Methods and Instruments

All chemicals used in this study were commercially available and used as received without any purification step taken. Chemicals namely sodium acetate (NaOAc), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium bicarbonate (NaHCO<sub>3</sub>) were purchased from R & M Supplier. In addition, 4-bromoacetophenone and methyl acrylate were procured by Sigma-Aldrich. N,N-dimethylacetamide (DMA) and other solvents were supplied by MERCK Chemical Co.

Gas chromatography analyses were carried on a Shimadzu 2010 equipped with a non-polar capillary column BP1 100% dimethylpolysiloxane, using Flame Ionization Detector. The micro-liter samples were injected at 15 °C. The temperature increment was set at 15 °C per minute and the final temperature was 300 °C.

### General Procedure for Catalytic Mizoroki-Heck Reaction.

A mixture of 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol), polystyrene-supported palladium(II) catalyst (0.01 mmol), sodium acetate (2.0 mmol) and DMA (5 mL) were mixed together in Radley's 12-placed reaction carousel whilst purged with nitrogen, stirred and refluxed at 120 °C for 1 and 3 hours (Scheme 1). The conversion of reactant was monitored by GC-FID. To identify the reaction products, the retention times of standards were used and the peak areas in the chromatograms were used to measure the product selectivity [9]. The Mizoroki-Heck reactions were then evaluated with three reaction parameters which are effect of different bases, catalyst loading and reaction temperature.

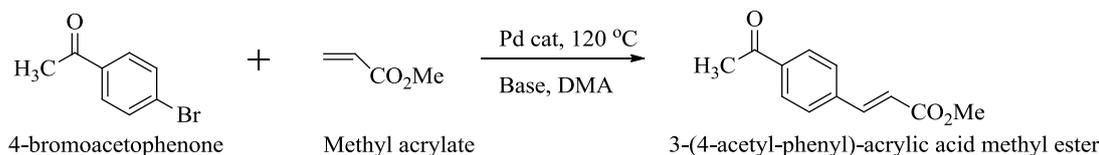


### Recyclability of the Supported Catalyst

After the catalytic reaction, the catalyst was separated, washed with acetonitrile to remove salts and organics residual and dried under vacuum. The catalyst was then subjected to the next reaction

### 3. Results and Discussion

Careful view into C-C coupling reaction process indicates that the reaction conditions have dramatic effects on the yield of the Mizoroki-



**Scheme 1:** General pathway for Mizoroki-Heck reaction of 4-bromoacetophenone with methyl acrylate.

Initial investigations have been explored to use different types of bases (Table 1). The reaction efficiency varied greatly according to the bases used. The inorganic bases such as sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ) and sodium acetate ( $\text{NaOAc}$ ) were examined as hydrogen halide neutralizer and remover [12]. The reaction yields were found to be strongly depend on the base employed and a remarkable increase in the product formation was observed in the presence of  $\text{NaOAc}$  (Table 1, entries 1 and 2).  $\text{NaOAc}$  leads quantitatively in 99% and 69%, respectively to the desired product. It was noted that the use of  $\text{Na}_2\text{CO}_3$  gave acceptable conversions of about 97% and 37% (Table 1, entries 3 and 4). In contrast, the inorganic base  $\text{NaHCO}_3$  was less effective. The lowest conversion was also observed for 40% and 57% (Table 1, entries 5 and 6) probably due to the insolubility of base in organic solvent.

**Table 1:** Effect of bases on the Mizoroki-Heck reaction<sup>a</sup>.

Entry	Base	Time (min)	Conversion <sup>b</sup> (%)
1	$\text{NaOAc}$	60	97
2	$\text{NaOAc}$	180	99
3	$\text{Na}_2\text{CO}_3$	60	37
4	$\text{Na}_2\text{CO}_3$	180	97
5	$\text{NaHCO}_3$	60	40
6	$\text{NaHCO}_3$	180	57

<sup>a</sup> Reaction conditions: the reactions were done in the present of supported catalyst (1.0 mmol%) in the coupling of 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol), base (2.0 mmol) in DMA (5.0 mL) at 120 °C, under  $\text{N}_2$  atmosphere.

<sup>b</sup> Determined by GC-FID

The influence of catalyst loading on the performance of Mizoroki-Heck was then examined using 0.25, 0.50 and 1.0 mmol% of supported catalyst (Table 2). The yields obtained normally depended on the amount of catalyst used. The catalytic reaction that can be carried out with a small amount of expensive catalyst is most efficient feature of synthetic reactions involving Pd(II) complex. So, by controlling the amount of used, high turnover number (TON) could be achieved to maximize the percentage conversion of the desired products. As shown in Table 2, the higher TON values 380 and 388 were achieved after 60 and 180 minutes of reaction times (Table 2, entries 5 and 6). Thus it can be concluded that the choice of 0.25 mmol% of supported catalyst is suitable since it gave the higher TON at the same reaction time compared to other catalyst loading

**Table 2:** Effect of catalyst loading on the catalytic performance.

Entry	Catalyst (mmol%)	Time (min)	Conversion <sup>b</sup> (%)
1	1.0	60	97 (97)
2	1.0	180	99 (99)
3	0.5	60	98 (196)

roki-Heck reaction [10,11]. Preliminary investigations were devoted to identify the optimal reaction conditions for Mizoroki-Heck reaction. As a model reaction, the coupling of 4-bromoacetophenone with methyl acrylate was screened for catalytic performance. The influence of different experimental conditions such as reaction temperature, amount of catalyst and bases were also optimized in the model reaction.

4	0.5	180	97 (194)
5	0.25	60	95 (380)
6	0.25	180	97 (388)

<sup>a</sup> Reaction conditions: the reactions were done in the present of 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol),  $\text{NaOAc}$  (2.0 mmol) in DMA (5.0 mL) at 120 °C, under  $\text{N}_2$  atmosphere.

<sup>b</sup> Determined by GC-FID

Values in parenthesis is turnover number (TON): mmol of product/mmol catalyst used

Under established the optimum catalytic conditions using  $\text{NaOAc}$  as a base with 0.25 mmol% of catalyst loading, the performance of supported catalyst was then screened at different reaction temperature, 100, 120 and 140 °C (Table 3). The reaction temperature has significant influence toward Mizoroki-Heck reaction [13]. Reaction temperature assists in the activation of aryl bromides. This parameter, however must be carefully controlled to avoid the deactivation of aryl bromides if the reaction temperature is too low. If the temperature is too high, the formation of palladium black is considered that encourage the inhibition of catalytic cycle [14]. On careful inspection of the data, the yields were gradually increased as the reaction temperature increase from 100 to 140 °C. The maximum conversion was achieved 100% at reaction temperature 140 °C (Table 3, entry 5). However, the percentage conversion of catalytic product at that temperature gave poor selectivity. Heidenreich et al., (2002) reported the higher temperature may cause the re-precipitation process and the palladium was less stable and easy to leach out into solution [15]. Also, the performing of reaction at 100 °C caused lower conversions than 120 °C. Consequently, the temperature at 120 °C remains as optimal reaction temperature to catalyse Mizoroki-Heck reaction.

**Table 3:** Effect of temperature on the catalytic performance.

Entry	Temperature (°C)	Time (min)	Conversion <sup>b</sup> (%)
1	100	60	8 (32)
2	100	180	54 (216)
3	120	60	95 (380)
4	120	180	97 (388)
5	140	60	100 (400)
6	140	180	98 (392)

<sup>a</sup> Reaction conditions: the reactions were done in the present of supported catalyst (0.25 mmol%) in the coupling of 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol),  $\text{NaOAc}$  (2.0 mmol) in DMA (5.0 mL) under  $\text{N}_2$  atmosphere.

<sup>b</sup> Determined by GC-FID

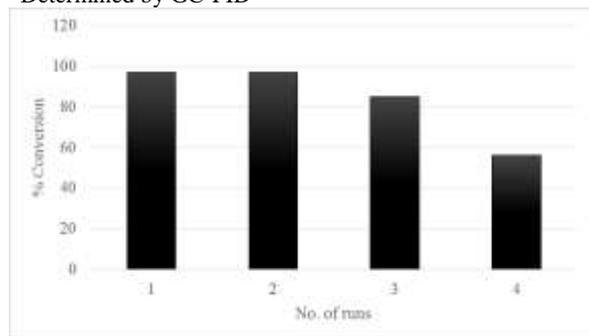
Values in parenthesis is turnover number (TON): mmol of product/mmol catalyst used

In final, a further set of experiments were carried out to determine the reusability of polystyrene-supported palladium(II) cata-

lyst for the Mizoroki-Heck reaction at 120 °C for 3 h. For each recycle, the catalyst was recovered from reaction mixture by simple filtration, washed several times with distilled water and acetonitrile, dried for half an hour and reused for the next run. As illustrated in Figure 1, the conversion of products slightly decreased due to the loss of catalyst activity after the catalyst was reused four times which might due to the palladium leached out from the support in the catalytic process.

<sup>a</sup> Reaction conditions: the reactions were done in the present of supported catalyst (0.25 mmol%) in the coupling of 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol), NaOAc (2.0 mmol) in DMA (5.0 mL) at 120 °C under N<sub>2</sub> atmosphere.

<sup>b</sup> Determined by GC-FID



**Figure 1:** Recycling studies of supported catalyst for the Mizoroki-Heck reaction.

## 4. Conclusion

In summary, supported palladium(II) complex could catalyse coupling reaction of 4-bromoacetophenone with methyl acrylate and the yields of products obtained were excellent. The use of synthesized supported palladium(II) complex as a heterogeneous catalyst for the Mizoroki-Heck reaction can simultaneously provide high activity and selectivity of final products, easy separation of catalyst and appropriate performance in the recycling reaction.

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