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### Communication

# Modified zeolite immobilized palladium for ligand-free Suzuki–Miyaura cross-coupling reaction

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#### ABSTRACT

A palladium-based catalyst supported on modified ZSM-5 was successfully prepared by a facile procedure. The prepared heterogeneous catalyst Pd@desilicated ZSM-5 showed an excellent catalytic activity at very low Pd loading (0.02 mol%) for the ligand-free Suzuki–Miyaura coupling reactions of various aryl bromides affording excellent yields of the products. The prepared catalyst presents good recyclability, over four catalytic cycles.

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#### 1. Introduction

Synthesis of biaryl and heteroaryl motifs has attracted considerable interest, as they are important building blocks for various natural products, herbicides, pharmaceuticals including antibiotic vancomycin and anticancer drug gossypol [1–3]. They are also present in many conducting polymers and liquid crystalline materials [4.5], and are synthesized using transition metal catalysis. Among the fundamental transition metal catalyzed transformations, palladium-catalyzed reactions, in particular, Suzuki-Miyaura coupling reaction is a powerful, versatile and popular tool for selective construction of carbon-carbon bonds in the synthesis of biaryls and heteroaryls from aryl halides or triflates with organoboron compounds [6–9]. The widely employed reaction protocol utilizes organic solvents in the presence of inorganic bases typically carbonates, and phosphane as a ligand. There is a growing recognition that more environmentally sustainable cross-coupling processes must be developed to replace current methodologies that are both material and energy intensive. In response, industry has begun adopting green chemistry practices to safer manufacturing processes. Among the various achievements on this issues, the development of ligand-free catalytic systems has been one of the most challenging fields, because they are the simplest and cheapest systems and more importantly, the "ligand-free" catalytic system makes it possible to carry out the reactions under an aerobic atmosphere and/or in an aqueous medium suppressing the phosphane-related side reactions [10-12].

Improved conditions have been developed for the Suzuki– Miyaura reaction, including the use of palladium nanoparticles, supported palladium, microwave technology, NHC-carbene ligands, ionic liquids, and so on [13–16]. Although considerable efforts have been made to develop metal–ligand catalytic systems that facilitate the Suzuki–Miyaura coupling, surprisingly little research has been performed on the ligand-free zeolite supported catalyst as compared to other support.

Recently Artok and co-workers found that Pd(II) exchanged NaY zeolite activates aryl halides in Suzuki–Miyaura reaction [17–19], while its mechanistic study was reported by Ryoo [20]. Djakovitch and Koehler [21] showed that, as modified zeolites possess large specific surface areas containing well-defined micropores and mesopores, the Pd complexes can be encapsulated within the cavity of zeolite framework with enhanced catalytic activity.

ZSM-5 zeolite is one of the zeolites that is well documented in the literature for isomorphous metal substitution in the framework as well as its high temperature behavior [22,23]. On the other hand it has been extensively studied for many organic transformations including support for metal catalysts [24–26]. In continuation of our work related to heterogeneous catalysis [27], herein we report a synthetic methodology to prepare Pd supported on modified ZSM-5 zeolite. The functionality of the introduced mesoporosity in the zeolite was demonstrated in a ligand-free Suzuki–Miyaura cross coupling reaction under aerobic conditions.





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Fig. 1. Scanning electron micrographs of a) ZSM-5, b) desilicated ZSM-5 and c) Pd@desilicated ZSM-5.



Fig. 2. EDS patterns of a) ZSM-5, b) desilicated ZSM-5 and c) Pd@desilicated ZSM-5.

#### 2. Results and discussion

Mesopores may be introduced into the zeolite crystals by a destructive chemical post-synthetic demetalation by means of selective extraction of Si or Al from the zeolite framework by dealumination and desilication methods [28-30]. Desilication is wellknown demetalation approach, which consists of the selective extraction of silicon atoms from the zeolite framework to yield lower Si/Al ratios with only small changes in framework properties [31,32]. Extraction of silicon atoms leads to a significant amount of extra porosity, with preserved structural integrity, depending on the mineralizing agent. Among the numerous methods available desilication by alkaline treatment has been demonstrated as an attractive top-down non-templating route to prepare modified zeolites having unique catalytic properties of the native micropores with improved transport consequence of a complementary mesopore network which has been recently explored and reviewed [33]. Generally, most of the zeolite frameworks contain more silicon than aluminum and accordingly one would more easily achieve the formation of extra pores by desilication process, leading to an interconnected network of micropores and mesopores which can be used for catalyst immobilization.

The immobilization of palladium in the modified ZSM-5 was performed in two steps. The first step is the desilication, which was carried out by treatment of commercial ZSM-5 (1) zeolite in 0.2 M sodium carbonate solution for 30 min to yield desilicated ZSM-5 (2). In the second step, the desilicated ZSM-5 was immersed in a THF solution containing  $Pd(OAc)_2$  for immobilization. The THF was removed by evaporation, and the zeolite sample was washed many times with diethyl ether to remove weakly adsorbed  $Pd(OAc)_2$  affording Pd@desilicated ZSM-5 catalyst (3). Inductively coupled

plasma (ICP) emission analysis showed a Pd content of 0.024 mmol  $g^{-1}$  in the resultant sample.

First the prepared materials were characterized by various techniques. Fig. 1 shows the SEM photographs of parent ZSM-5, desilicated ZSM-5 and Pd@desilicated ZSM-5. As can be seen, for all no observable change in the particle size and surface



Fig. 3. XRD patterns of a) ZSM-5, b) desilicated ZSM-5 and c) Pd@desilicated ZSM-5.



Fig. 4. TGA plot of Pd@desilicated ZSM-5.

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Scheme 1. Pd@desilicated ZSM-5 catalyzed Suzuki-Miyaura coupling reaction.

morphology were observed. All the three materials had a uniform particle size of 0.5–1.2  $\mu m$  with irregular shape.

Energy dispersive X-ray spectroscopic (EDS) elemental analysis (Fig. 2) revealed the decreased overall Si/Al ratios from 28.40 (ZSM-5) to 24.40 (desilicated ZSM-5) which confirmed the preferred silicon extraction occurred during desilication process. It also confirmed the existence of Pd in the zeolite framework.

Powder XRD patterns of the three materials are displayed in Fig. 3 which confirmed the phase purity and retention of crystallinity after alkaline treatment. Simple visual inspection of the diffractograms shows that all three samples consist of highly crystalline MFI phase. The appearance of reflections in the XRD pattern due to Pd phase is far away from the detection limit of the sensitivity of the detector used in the present study (detection limit

The effect of base and solvent on the Suzuki-Miyaura cross-coupling reaction.<sup>a</sup>

Entry	Base	Solvent	Time (h)	Yield <sup>b</sup> (%)
1	K <sub>2</sub> CO <sub>3</sub>	EtOH	2	96
2	Na <sub>2</sub> CO <sub>3</sub>	EtOH	2	93
3	K <sub>3</sub> PO <sub>4</sub> .3H <sub>2</sub> O	EtOH	2	78
4	NaOAc	EtOH	4	72
5	K <sub>2</sub> CO <sub>3</sub>	MeOH	2	94
6	K <sub>2</sub> CO <sub>3</sub>	Toluene	6	70
7	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	6	69
8	K <sub>2</sub> CO <sub>3</sub>	$CH_2Cl_2$	6	69
9	K <sub>2</sub> CO <sub>3</sub>	THF	3	75
10	K <sub>2</sub> CO <sub>3</sub>	DMF	6	30
11	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	8	10

 $^{\rm a}$  Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst **3** (0.5 mol%), base (2.0 mmol), solvent (5 mL) at 80  $^\circ \rm C$  under aerobic conditions.

<sup>b</sup> Isolated yields after purification.

Table 1

5% by weight). However, the decrease in the intensity of the reflections of desilicated ZSM-5 after loading of Pd reveals that the charge balancing counter cations slightly decelerate the intensities.

It is already reported that desilication of ZSM-5 resulted into mesopore formation accompanied with enhanced surface area [34]. N<sub>2</sub> adsorption measurements confirmed that an increase in surface area of zeolite from 270 m<sup>2</sup> g<sup>-1</sup> (ZSM-5) to 368 m<sup>2</sup> g<sup>-1</sup> (desilicated ZSM-5) as a consequence of the base treatment. After the immobilization of Pd in desilicated ZSM-5 the surface area is reduced to 314 m<sup>2</sup> g<sup>-1</sup> (Pd@desilicated ZSM-5) due surface being covered with Pd.

TGA analysis was carried out to investigate the thermal stability of the catalyst and is shown in Fig. 4. The sample was scanned in the range of 25–1000 °C. Weight loss is mainly divided into two temperature regions: below 100 °C and 200–300 °C. Weight loss

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ct of the amount of catalyst on the Suzuki-Miyaura cross-coupling reaction.

Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	Yield <sup>b</sup> (%)
1	3	0.5	2	96
2	3	0.2	2	96
3	3	0.1	2	95
4	3	0.05	2	95
5	3	0.02	2	96
6	Pd@ZSM-5	0.02	3	80
7	Pd(OAc) <sub>2</sub> /TPP	0.02	10	30

 $^a\,$  Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst  ${\bf 3}$  (0.5–0.02 mol%), K\_2CO\_3 (2.0 mmol), ethanol (5 mL) at 80 °C under aerobic conditions.

<sup>b</sup> Isolated yields after purification.

Table 3

The effect of temperature on the Suzuki-Miyaura cross-coupling reaction.<sup>a</sup>

Entry	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)
1	rt	12	0
2	50	2	40
3	70	2	74
4	80	2	96

 $^a$  Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst  ${\bf 3}$  (0.02 mol%), K\_2CO\_3 (2.0 mmol), ethanol (5 mL) at 80 °C under aerobic conditions.

<sup>b</sup> Isolated yields after purification.

 Table 4

 The Suzuki–Miyaura cross-coupling reaction of aryl bromides and arylboronic acids.<sup>a</sup>

Entry	Aryl halide	Arylboronic acid	Product	Time (h)	Yield <sup>b</sup> (%)
1	Br	BOH) <sub>2</sub>		2	96
2	Br F	BOH) <sub>2</sub>	F	2	94
3	Br	BOH) <sub>2</sub>		2	92
4	Br CHO	BOH) <sub>2</sub>	СНО	2.5	80
5	Br	BOH) <sub>2</sub>		2	89
6	Br	BOH) <sub>2</sub>		2.5	93
7	O Br	BOH) <sub>2</sub>		2	94
8	Br	BOH) <sub>2</sub>		4	55
9	Br OCH <sub>3</sub>	BOH) <sub>2</sub>	H <sub>3</sub> CO	2.5	91
10	Br CH <sub>3</sub>	BOH) <sub>2</sub>	H <sub>3</sub> C	2.5	90
11	CI	BOH) <sub>2</sub>		8	39
12	C CI	BOH) <sub>2</sub>		9	41

#### Table 4 (continued)



Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), catalyst 3 (0.02 mol%), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), ethanol (5 mL) at 80 °C under aerobic conditions. <sup>b</sup> Isolated yields after purification.

during heating from 25 to 100 °C was assigned to the loss of loosely surface bound water (3.5%). The weight loss of around 5.0% at temperature between 100 and 300 °C was due to the loss of water and organics encapsulated in the cavity of support.

The activity of prepared catalyst was evaluated against the Suzuki-Miyaura coupling reaction. At the outset, we chose bromobenzene 4 and phenylboronic acid 5 as a model reaction partners (Scheme 1) to evaluate the effects of various reaction conditions such as base, solvent, catalyst loading and temperature on the reaction.

The reaction was initially performed using 0.5 mol% catalyst and K<sub>2</sub>CO<sub>3</sub> as base in ethanol. High conversion was obtained at 80 °C in 2 h (Table 1, entry 1). Various bases were screened and it was apparent that carbonate bases were more effective in activating the catalyst as compared to the other bases. Screening of solvents indicated that ethanol was the best solvent for this system. A catalyst allowed >69% product yield for all other solvents, while widely used DMF and 1,4-dioxane resulted in only 30% and 10% yields of the product with prolonged reaction time (Table 1, entries 10 and 11). Use of ethanol renders this protocol guite practical and amenable to large scale synthesis.

Effect of catalyst concentration on the percentage conversion of the product of **4** and **5** has been studied and the results are shown in Table 2. It was reported that the activity of Pd catalyst improves upon lowering the Pd loading in ligand-free cross coupling reactions [35]. Similar results were observed in this case also, and among the different loadings 0.02 mol% proved to be the best affording desired product in 2 h with 96% yield. For comparison the model reaction was performed with Pd@ZSM-5 under the established condition. It was observed that Pd@ZSM-5 was less active than Pd@desilicated ZSM-5 (Table 2, entry 6). This fact demonstrated that, introduced mesoporosity in zeolite framework leads to higher catalytic activity, due to the improved accessibility of the molecules to the active sites in 3. To compare the catalytic activity of free and immobilized Pd(OAc)<sub>2</sub> the reaction of Pd(OAc)<sub>2</sub>/TPP (Table 2, entry 7) was carried out in EtOH at 80 °C. The catalyst 3 showed considerable higher activity than Pd(OAc)<sub>2</sub>/TPP, this is probably due to better stabilization of the active Pd by the zeolite framework.

To study the effect of temperature on catalytic activity, the model reaction was carried out at room temperature (Table 3). The reaction did not occur at room temperature (Table 3, entry 1) indicating that the reaction temperature is crucial to the catalytic efficiency. Increasing the reaction temperature from room temperature to 70 °C, the yield of the product was increased slowly from 0 to 74%, while remarkable rate acceleration was observed at 80 °C, affording a quantitative yield of the desired product (Table 3, entry 4).

Next, the scope of the catalyst was explored with a range of aryl bromides and arylboronic acids under the conditions of 0.02 mol% catalyst in ethanol at 80 °C using K<sub>2</sub>CO<sub>3</sub> as a base. As shown in Table 4, in general, all reactions provided the biaryl derivatives in good to excellent yields. Importantly, the catalyst 3 was also applicable to a sterically hindered aryl halide, 2,4,6trimethylbromobenzene resulted in 55% yield in 4 h (Table 4, entry 8). Despite the economical advantages of employing aryl chlorides in the Suzuki-Miyaura reaction, an electron neutral chlorobenzene resulted in a 39% yield (Table 4, entry 11), and a moderate yield was obtained with an activated chloroarenes (Table 4, entries 12 and 13).

In order to evaluate the heterogeneity of catalyst, hot filtration test was performed by coupling bromobenzene with phenylboronic acid under the optimized conditions. After 50% of the crosscoupling reaction was completed (1 h, GC), the catalyst was filtered off and filtrate was allowed to react further. No further reaction was observed even after a prolonged reaction time suggesting that the palladium catalyst remains on the support during the reaction as reported for NaY zeolite [21].

According to Gladysz TON is more important for a catalyst than its recyclability for practical applications [36]. As our system worked with very low Pd loading (0.02 mol%) with high TON, more than 100 recycles would be needed for high Pd loaded catalyst to match the effectiveness of our catalyst in terms of TON values. The reusability test of the catalyst was examined in case of the model reaction between bromobenzene and phenylboronic acid under optimized reaction condition. The yield of the product decreases in the subsequent uses (Ist 96%, IInd 89%, IIIrd 86%, IVth 82%), it may be due to the loss of the catalyst by tricky separation of the small amount of the catalyst employed from the reaction mixture.

#### 3. Conclusion

In conclusion, modified ZSM-5 zeolite was used as a support for immobilization of Pd. We have demonstrated the utility of the prepared catalyst Pd@desilicated ZSM-5 in the ligand-free Suzuki-Miyaura coupling reactions of various aryl bromides with arylboronic acids in ethanol with relatively low Pd-loading in shortest reaction times. In terms of green chemistry, the process is of great interest because waste generation is largely minimized in the absence of added ligand and as of a very low Pd loading. The prepared catalyst presents good recyclability, over four catalytic cycles.

#### 4. Experimental

#### 4.1. General remarks

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AC (300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR) spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. A JEOL-6360 scanning electron microscope was used for SEM observations and energy dispersive X-ray spectroscopy (EDS) analysis. TGA-DTA analysis was recorded on SDS Q600 N20.9 in air. All the chemicals were obtained from Aldrich, Spectrochem and were used without further purification.

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#### 4.2. Typical procedure for preparation of desilicated ZSM-5 (2)

In a typical experiment, ZSM-5 (1.0 g) was treated with 0.20 M Na<sub>2</sub>CO<sub>3</sub> solution (about 30 mL/g) for 3 h at 75 °C. After the first 3 h period followed by washing with deionized water for 1 h at 75 °C, the sample was filtered and then submitted to another 3 h of treatment with a fresh Na<sub>2</sub>CO<sub>3</sub> solution of the same concentration. The solid was filtered and washed several times with distilled water. The desilicated zeolite was washed at 80 °C with stirring in distilled water (3 × 30 mL) to complete remove sodium silicate from the medium, and finally, dried at 120 °C, which yielded 0.80 g white powder (**2**).

#### 4.3. Immobilization of $Pd(OAc)_2$ onto desilicated ZSM-5 (3)

In a 50 mL Schlenk tube containing a desilicated ZSM-5 (1.0 g) in dry THF (20 mL) was added dropwise solution of  $Pd(OAc)_2$  (0.022g, 0.01 mol) at room temperature. The mixture was stirred for 48 h at room temperature, the solvent was removed by evaporation and the resultant solid was washed with diethyl ether (3 × 5 mL). Then the obtained zeolite was allowed to dry at room temperature to afford 0.90 g of Pd@desilicated ZSM-5 (**3**).

## 4.4. Typical experimental procedure for the Suzuki–Miyaura reaction

In a typical procedure 50 mL Schlenk tube containing magnetic stirring bar and equipped with reflux condenser was charged aryl bromide (1.0 mmol), arylboronic acid (1.2 mmol),  $K_2CO_3$  (2.0 mmol), and 0.009 g catalyst (0.02 mol%) in ethanol (5 mL). The reaction mixture was vigorously stirred at 80 °C. After completion of the reaction as monitored by TLC, the catalyst was separated out by filtration, followed by washing with water and diethyl ether. The filtrate was extracted with diethyl ether (3 × 10 mL). The combined organic layers were collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to afford crude product, which was purified by silica gel column chromatography (*n*-hexane:EtOAc = 9:1).

#### 4.5. Spectral data of representative compounds

#### 4.5.1. 4-phenyl benzophenone (Table 4, entry 7)

White solid, mp 99–100 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.35–7.40 (m, 1H), 7.46–7.54 (m, 4H), 7.58 (d, 1H, *J* = 1.5 Hz), 7.60– 7.64 (m, 2H), 7.71 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 2H, *J* = 8.4 Hz), 7.92 (d, 2H, *J* = 8.4 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 126.6, 127.0, 128.1, 128.2, 128.8, 129.9, 130.4, 131.9, 136.0, 137.9, 140.1, 144.9, 196.0; MS (ESI): *m/z* 258.

#### 4.5.2. 2,4,6-trimethylbiphenyl (Table 4, entry 8)

Colorless liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 2.27 (s, 3H), 2.43 (s, 6H), 6.92 (d, 2H, *J* = 2.5 Hz), 7.15–7.17 (m, 1H), 7.34–7.48 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 20.6, 23.9, 127.0, 128.0, 128.4, 128.6, 129.0, 129.3, 135.6, 136.0, 136.3, 137.9; MS (ESI): *m/z* 196.

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