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# Silica-supported terpyridine palladium(II) complex as an efficient and reusable catalyst for Heck and Suzuki cross-coupling reactions

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Silica-supported terpyridine palladium(II) was prepared and used as an effective and recyclable catalyst in Mizoroki–Heck and Suzuki–Miyaura coupling reactions. The catalyst was very effective for the Mizoroki–Heck reaction of aryl halides with olefins and conversion was in most cases excellent. The catalyst showed good thermal stability (up to 230 °C) and could be recovered and reused for four reaction cycles. The Suzuki coupling of aryl iodides with aryl boronic acids in the presence of the catalyst was also investigated and the reaction proceeded with a short reaction time and excellent conversion. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: Mizoroki-Heck reaction; Suzuki-Miyaura reaction; heterogeneous catalyst

### Introduction

Coupling reactions, including Mizoroki–Heck and Suzuki–Miyaura reactions, provide single operational methods to form a new carbon–carbon (Csp<sup>2</sup>—Csp<sup>2</sup>) bond in modern synthetic chemistry, and they have emerged as powerful tools in both academic and industrial laboratories.<sup>[1–3]</sup> The Heck reaction enables the direct cross-coupling of simple alkenes with aryl or vinyl halides. The cross-coupling reactions of aryl halides with arylboronic acids, often referred to as Suzuki coupling reactions, are versatile methods for synthesizing unsymmetrical biaryls, which have a crucial role in natural products and pharmaceutical compounds.<sup>[4–6]</sup> These coupling reactions have recently been considered because of their appropriate application in total synthesis without protecting groups and their potential to simplify functionalization of the aryl group.<sup>[1–3]</sup>

These coupling reactions were mostly carried out by homogeneous palladium complexes, which cause difficulties in the purification of the final product, recycling of the catalyst and deactivation via aggregation into palladium nanoparticles. These problems are of environmental and economic concern in largescale synthesis in industry.<sup>[2,7,8]</sup>. From industrial, economic and environmental points of view, the development of a less expensive, efficient and environmentally benign catalyst is still in high demand. In this context, the continued development of reusable heterogeneous catalysts can potentially reduce both cost and waste.<sup>[9-13]</sup> A number of organic compounds, such as organic polymers and carbonaceous material, inorganic compounds (such as silica, zeolites and metal oxides) and hybrid organicinorganic materials (mainly grafted silica) have been used as supports for palladium nanoparticles. Alternatively, the grafting of such supports with homogeneous catalysts often provides good catalytic activity as well as possible recovery of the catalyst system by simple conduction.<sup>[8–13]</sup>

Recently, the terpyridines, as tridentate ligands with efficient and stable chelating ability to transition metals, have received increasing attention.<sup>[14–21]</sup> Terpyridine nickel complexes have

been used to catalyze alkyl cross-coupling reactions.<sup>[14]</sup> The Suzuki–Miyaura cross-coupling reaction has been reported in the presence of polymer-supported terpyridine palladium complex,<sup>[15]</sup> and the SBA-15-supported iron terpyridine complex has been used to catalyze oxidative C—C cross-coupling reactions of tertiary amines with carbon nucleophiles.<sup>[16]</sup> Very recently, we have reported the synthesis of terpyridine-functionalized MCM-41 nanoporous silica for the removal of chromate in the environment.<sup>[22]</sup> Herein we wish to describe the synthesis of silica-supported terpyridine palladium(II) complex (silica-terpy–Pd(II)) and demonstrate its catalytic activity in Mizoroki–Heck and Suzuki–Miyaura reactions. Silica as an inorganic support has several advantageous, such as excellent stability, good accessibility and the fact that organic groups can be robustly anchored to the surface.<sup>[12]</sup>

### Experimental

### Preparation of 3-Aminopropyl Triethoxysilane-Functionalized Silica (APS)

Silica (with an average pore diameter of 60 ) was activated by refluxing in hydrochloric acid (6 m) for 24 h and then washing thoroughly with deionized water to neutral pH and drying before carrying out surface modification. The activated silica (5.0 g) and 3-aminopropyltriethoxysilane (1.65 mmol) in dry toluene was stirred under reflux conditions for 24 h. The solid material was filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhlet) and then dried in an oven at 110 °C overnight to give APS.

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### Preparation of Terpyridine-Functionalized Silica (SiO<sub>2</sub>-Terpy) 5

The resulting APS (5.0 g) was reacted with terephthalaldehyde (10 mmol) in methanol under reflux conditions for 24 h. The solid material was filtered off and washed with MeOH, CHCl<sub>3</sub> and DMF to afford imino-functionalized silica **2**. The imino-functionalized silica **2** was added to a mixture of 2-acetylpyridine (10 mmol) and NaOH (0.5 g, pH 11) in ethanol and refluxed for 24 h. Then NH<sub>4</sub>OAc (100 mmol) was added to the reaction mixture and refluxed for a further 24 h. The solid was filtered off and washed with toluene, MeOH, DMF, DMSO and water. The resulting material was dried in an oven at 110 °C for 8 h.

## Preparation of Palladium(II) Complex Supported on Terpyridine-Functionalized Silica 6

The catalyst was prepared by stirring a mixture of SiO<sub>2</sub>–Terpy **5** (2.0 g) and palladium acetate (0.96 mmol) in dry acetone (25 ml) at room temperature. After stirring for 24 h, the resulting brown solid was filtered and washed with acetone and dichloromethane. Finally, the material was dried at 90 °C for 6 h.



Scheme 1. Synthesis of catalyst.



Figure 1. IR spectrum of (a) silica-terpy and (b) silica-terpy-Pd.

#### **General Experimental Procedure for the Heck Reaction**

The catalyst (1.0 mol%) and  $K_2CO_3$  (1.2 mmol) was stirred in *N*-methyl-2-pyrrolidone (NMP) (2.0 ml) for 10 min. Then aryl halide (1.0 mmol) and olefin (1.0 mmol) were added and magnetically stirred for an appropriate time (Table 2) at 100 °C. After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was separated by filtration. Conversions and yields of the reactions were determined by gas chromatography (GC).

### General Experimental Procedure for the Suzuki Reaction

The catalyst (1.0 mol%) and  $K_2CO_3$  (1.2 mmol) were stirred in H<sub>2</sub>O (2 ml) for 10 min. Then aryl halide (1.0 mmol) and boronic acid (1.0 mmol) were added and magnetically stirred for 0.5–1.5 h at 90 °C. After cooling the reaction mixture to room temperature, the catalyst was separated by filtration. Ethyl acetate (2×5 ml) was added to the filtrate. The organic layer was separated and dried with MgSO<sub>4</sub>. Conversions and yields of the reactions were determined by GC.

### **Results and Discussion**

### Synthesis of Silica-Terpy-Pd(II) Complex

Preparation of the catalyst is outlined in Scheme 1. The activated silica was functionalized with 3-aminopropyltriethoxysilane, followed by condensation with terphthalaldehyde **1** using known procedures<sup>[23]</sup> to give the corresponding aldehyde-functionalized silica **2**. The iminofunctionalized silica **2** was subsequently reacted with 2acetylpyridine **3** in alkaline conditions to afford bis-pyridylfunctionalized silica **4**. Amorphous silica-supported terpyridine (SiO<sub>2</sub>-terpy) **5** was prepared via the reaction of **4** and NH<sub>4</sub>OAc in EtOH under reflux conditions similar to the mesoporous silica counterpart.<sup>[21]</sup> The obtained SiO<sub>2</sub>-Terpy **5** was then reacted with an acetone solution of Pd(OAc)<sub>2</sub> at room temperature to afford the silica-supported terpyridine palladium(II) complex (silica-terpy-Pd(III)) **6**.

Table 1. Optimization of Mizoroki–Heck reaction <sup>a</sup>										
Ph-I + $\int_{1}^{1} CO_2 Me$ Solvent, Cat. Ph $K_2 CO_3, 100 \circ C$ CO <sub>2</sub> Me										
Entry	Solvent	Catalyst (mol%)	Time (h)	Conversion (%) <sup>b</sup>						
1	H <sub>2</sub> O	1	1	46						
2	NMP	1	1	88						
3	DMF	1	2	63						
4	Toluene	1	2	33						
5	NMP	0.5	1	58						
6	NMP	0.8	1	76						
7	NMP	1.2	1	85						
8	NMP	1	1	74 <sup>c</sup>						
9	NMP	1	1	89 <sup>d</sup>						

<sup>a</sup>Reaction conditions: Ph–I (1 mmol), methyl acrylate (1 mmol),  $K_2CO_3$  (1.2 mmol), catalyst (based on content of Pd). <sup>b</sup>% conversion determined by GC.

<sup>c</sup>Reaction temperature = 80 °C.

<sup>d</sup>Reaction temperature = 120 °C.

The IR spectrum of **2** showed two adsorption peaks at 1706 and 1646 cm<sup>-1</sup> (SI), ascribed to aldehyde and imine groups, respectively. This clearly confirms the functionalization of silica by terphthalaldehyde. Bands at  $1060 \text{ cm}^{-1}$  in the IR spectrum of **5** were assigned to the symmetric stretching vibration of Si—O<sup>[24]</sup> (Fig. 1). The peaks of the organic groups were relatively weak because of their low content in functionalized silica. Bands observed at  $1644 \text{ cm}^{-1}$  for **5** could be attributed to the C=N (pyridine ring) stretching frequency.<sup>[11]</sup>. The C=N bands of complex **6** were shifted to a lower frequency in the IR spectrum ( $1619 \text{ cm}^{-1}$ ) compared to that of **5**. The lowering in frequency of the C=N peak is indicative of the formation of a metal–ligand bond.

From the TGA of **5** (SI), loading of the terpyridine ligand that bound to the silica surface was calculated to be 0.48 mmol g<sup>-1</sup>, in accordance with CHN analysis. The loading of palladium in **6** was determined to be 0.12 mmol g<sup>-1</sup> by atomic adsorption spectroscopy. In order to obtain an insight into the oxidation state and coordination environment of palladium in silicaterpy–Pd(II), X-ray photoelectron spectroscopy (XPS) was performed (SI). The Pd 3d5/2 and Pd 3d3/2 binding energies were determined to be 337.0 and 342.2 eV, respectively. These values correspond to the Pd(II) binding energy of silica-terpy– Pd(II) complex.

Table 2. Heck coupling of aryl halides with olefins										
$ \begin{array}{c}                                     $										
Entry	Х	R <sub>1</sub>	R <sub>2</sub>	Time (h)	Conversion (%) <sup>a</sup>	Yield (%) <sup>a</sup>				
1	I	Н	CO <sub>2</sub> Me	1	88	83				
2	I	Н	CO <sub>2</sub> Et	2:5	87	81				
3	I	Н	CO <sub>2</sub> Bu	1.2	80	75				
4	I	Me	CO <sub>2</sub> Me	2	89	84				
5	I	COMe	CO <sub>2</sub> Et	4	96	90				
6	Br	NO <sub>2</sub>	CO <sub>2</sub> Me	3	97	88				
7	Br	NO <sub>2</sub>	CO <sub>2</sub> Et	8	95	91				
8	Br	СНО	CO <sub>2</sub> Et	3	98	91				
9	Br	Н	CO <sub>2</sub> Bu	20	61	53				
10	Br	СНО	CO <sub>2</sub> Bu	9	82	78				
11	Br	NO <sub>2</sub>	CN	20	87	63				
12	Br	Me	CO <sub>2</sub> Me	9	77	71				
13	Cl	NO <sub>2</sub>	CO <sub>2</sub> Me	24	72	65				
14	Cl	NO <sub>2</sub>	CO <sub>2</sub> Bu	35	80	75				
15	Cl	CO <sub>2</sub> H	CO <sub>2</sub> Me	32	96	92				
16	Cl	2,4-NO <sub>2</sub>	CO <sub>2</sub> Me	20	95	88				
17	L	Н	Ph	5	52	48				
18	L	CO <sub>2</sub> Me	Ph	6	74	69				
19	Br	NO <sub>2</sub>	Ph	8	54	49				

<sup>a</sup>% Determined by GC.

### Catalytic Activity of Silica-Terpy-Pd(II)

The catalytic activity of silica–terpy–Pd(II) **6** for Mizoroki–Heck reaction was investigated. The coupling reaction of iodobenzene with methyl acrylate was used as a model reaction to determine the optimum reaction conditions in the presence of  $K_2CO_3$  as a base (Table 1). NMP was the solvent of choice, and using it in the reaction resulted in a high yield after 1 h. To study the effect of the amount of catalyst, the reactions were carried out at different amounts of **6** ranging from 0.5 to 1.2 mol%. It was found that by increasing the amount of catalyst from 0.5, 0.8 and 1.0 to 1.2 mol%, the yield increased from 58%, 76%, and 88% to 85%, respectively. Furthermore, results showed that 1 mol% catalyst in NMP was sufficient to push this reaction forward. Further increases in the amount of catalyst did not improve the yield. As can be observed from Table 1, the most suitable reaction temperature was 100 °C.

To verify the effectiveness and generality of the catalyst and procedure, the reaction of various aryl halides and olefins were examined under optimized reaction conditions (Table 2). It is known that the catalyst is very effective for reactions with aryl iodides and aryl bromides as arylating agents. For all of the olefins that were examined, good conversion and yield were achieved. Aryl chlorides have not typically been used in the Heck reaction because oxidative addition occurs more easily with bromides and iodides. However, the use of aryl chlorides is highly desirable, as they are more cost effective and readily available over alternative reagents. Therefore, we studied the Heck reaction with aryl chlorides under the same reaction conditions. The catalytic system was able to affect the Heck coupling reaction of aryl chlorides, and good conversions and yields could be obtained after 20-35 h (entries 13–16). Reactions involving aryl iodides or bromide gave moderate conversions and yields with styrene (entries 17-19).

The recyclability of the silica–terpy–Pd(II) catalyst was also examined by the coupling reaction of iodobenzene and methyl acrylate as a test model. After completion of the reaction, the catalyst was filtered and then washed with DMF, CHCl<sub>3</sub> and water. The recovered catalyst was dried at 100 °C for 5 h and then reloaded with fresh reagents for further runs. Recovery was achieved in four successive reaction runs (Fig. 2). To determine whether the catalyst was actually functioning in a heterogeneous manner or whether it was merely a reservoir or more active soluble palladium species, we performed a hot filtration test<sup>[25]</sup> after the reaction of iodobenzene with methyl acrylate initiates and before the substrates were consumed. The hot filtrates were then transformed to



reaction times= 1 hour.

**Figure 2.** Reusability of catalyst in the Heck reaction. Reaction time = 1 h.

another flask containing  $K_2CO_3$  in NMP at 100 °C. Upon further heating of the catalyst-free solution for 2 h, no considerable progress (~10% by GC analysis) was observed.

Finally, the catalyst was tested in the Suzuki coupling reaction. The Suzuki coupling of aryl iodides with aryl boronic acids in the presence of the silica–terpy–Pd(II) catalyst (1 mol%) using  $K_2CO_3$  as a base in water under stirring at 90 °C was also investigated and the reaction proceeded with a short reaction time (0.5–1.5 h), with excellent conversion and yield (Table 3). Under the same reaction conditions the coupling of chlorobenzene and bromobenzene failed to provide the target products.

Recyclability of the catalyst was also examined in the model reaction of iodobenzene and phenylboronic acid. As shown in Fig. 3, recovery was achieved in four successive reaction runs. To check whether palladium was being leached out from the solid support to the solution, a typical hot filtration test was performed in the model reaction. After continuing the reaction for 0.5 h, the catalyst was removed by filtration and the determined conversion was 40%. The resulting filtrate was subjected to heating for a further 2 h. From the GC results it was revealed that after separation of the catalyst no conversion took place in the filtrate. Since no further conversion was observed, this indicates that soluble species may not be involved in the reactions.





Figure 3. Reusability of catalyst in the Suzuki reaction. Reaction time = 1.5 h.

### Conclusion

Silica-supported terpyridinepalladium(II) complex as an active catalyst has been developed for Mizoroki–Heck and Suzuki–Miyaura coupling reactions. This catalyst was recovered and reused four times with decreasing activities.

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