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Graphical Abstract



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Synthesis, characterization, and application of palladium-dithizone immobilized on magnetic nanoparticles as an efficient and recoverable catalyst for Suzuki type coupling reactions

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ABSTRACT

A novel, magnetically separable catalyst was synthesized by the immobilization of Pd on magnetite nanoparticles (MNPs) coated with dithizone. The activity of this catalyst was examined for the synthesis of various biaryls via the C-C coupling reaction of aryl halides and sodium tetraphenylborate or phenylboronic acid under mild reaction conditions. Fe₃O₄/SiO₂-DTZ-Pd was characterized by transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, vibrating sample magnetometer and scanning electron microscopy.

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1. Introduction

Sodium tetraphenylborate Phenylboronic acid

Catalysts and catalytic reactions have attracted significant attention in industrial applications and fundamental research.¹ In recent years, effort in catalysis research have been allocated to the application of useful and safe heterogeneous catalysts.² Heterogeneous catalysts are more efficient than homogeneous catalysts because of their recyclability.^{3,4} However, some heterogeneous palladium catalysts have low reactivity because of leaching from the support.^{5,6} Thus, the design of new heterogeneous catalysts that retain the activities and selectivity of homogeneous catalysts is important.⁷ In the past few years, among various solid supports, Fe₃O₄ has shown high-performance due to its unusual magnetic properties, high stability and recoverability with an external magnet.⁸ Because of the widespread applications in biotechnology, biomedical, material science, and environmental fields, much attention has been paid to the synthesis of different functionalized magnetic nanoparticles (MNPs).9-12

The Suzuki-Miyaura cross-coupling between aryl halides and organoboranes represents one of the most efficient methods for synthesis of biaryls.¹³ Substituted biaryl compounds have considerable application for the synthesis of biologically active substances such as pharmaceuticals and herbicides.^{14,15} Boronic acids, which are stable to air and moisture with low toxicity are Scheme 1. Synthesis of Fe₃O₄/SiO₂-DTZ-Pd typically used in the Suzuki-Miyaura reaction.¹⁶ Sodium

tetraphenylborate and phenylboronic acid are two stable and commercially available reagents which have been utilized for the Suzuki-Miyaura reaction. It has been reported that all four phenyl groups of sodium tetraphenylborate can be coupled with aryl halides to efficiently generate the product.17

The work herein, details the synthesis and characterization of a novel MNPs-supported Pd-dithizone complex and its use in the Suzuki-Miyaura coupling reaction of sodium tetraphenylborate or phenylboronic acid with variety of aryl halides. This catalyst could be readily recovered from the reaction mixture by application of an external magnet.



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2. Results and Discussion

The MNPs/SiO₂-DTZ-Pd complex was synthesized according to Scheme 1. Initially, Fe_3O_4 was formed *via* the chemical coprecipitation of Fe^{2+} and Fe^{3+} in basic solution. Following this, the MNPs were coated with 3-(chloropropyl)triethoxysilane. Then, dithizone-functionalized Fe_3O_4 were synthesized by the reaction of chloro-functionalized MNPs and diphenylthiocarbazone. Finally, palladium was bonded to the MNPs/SiO₂-DTZ surface.

The morphology and size of the MNPs/SiO₂-DTZ-Pd complex was investigated using scanning electron microscopy (SEM) (ESI, Fig. S1a) and transmission electron microscopy (TEM) (ESI, Fig. S2). TEM micrographs confirmed the spherical shape of Fe_3O_4 . The energy dispersive X-ray spectroscopy (EDS) spectrum of the MNPs/SiO₂-DTZ-Pd (ESI, Fig S1b) clearly showed the presence of Pd in the magnetic nanoparticles. The distribution of the elements (atomic percent) in the complex was determined as Si = 1.49%, Fe = 29.15%, O = 62.38% and Pd = 5.59%. Fourier transform infrared (FT-IR) spectra of the Fe₃O₄ nanoparticles (MNPs) (pink curve), chloro-functionalized MNPs (blue curve), MNPs-DTZ (green curve) and MNPs/SiO₂-DTZ-Pd (red curve) are shown in ESI, Fig S3. The pink curve showed characteristic peaks at 3399 cm⁻¹ due to stretching of the O-H bonds which were attached to the surface of the MNPs and a sharp peak at 580 cm⁻ due to vibrations of the Fe–O bond. Peaks at 997and 1044 cm⁻¹ in the IR spectrum of the chloro-functionalized MNPs were assigned to the Si-O stretching vibrations. The NH group of MNPs-DTZ was observed at 3397 cm⁻¹, while the NH group of MNPs/SiO₂-DTZ Pd appeared at 3438 cm⁻¹, indicating the attachment of Pd on the surface of MNPs-DTZ. An XRD spectrum of the prepared MNPs/SiO₂-DTZ-Pd was collected and six characteristic peaks (20=30.1°, 35.3°, 43.0°, 53.4°, 56.9° and 62.5°) were observed as well as three characteristic peaks ($2\theta=39.3^{\circ}$, 45.9° and 67.1°), related to formation of the structure of Pd NPs. The magnetic properties of samples containing a magnetite component were studied using a vibrating sample magnetometer (VSM) at room temperature. The saturation magnetization of MNPs/SiO2-DTZ Pd was determined as 51.6 emu/g (ESI, Fig. S5a). A comparison with the VSM of Fe₃O₄ (Fig. S5b) indicated that the magnetization of Fe₃O₄ was considerably decreased upon coating the organic layers on the surface of the magnetic nanoparticles.¹

The catalytic activity of MNPs/SiO₂-DTZ-Pd was explored in the Suzuki coupling reaction. To develop optimal reaction conditions, the reaction of iodobenzene with sodium tetraphenylborate or phenylboronic acid was explored as a model reaction. The exact loading of Pd on the magnetic nanoparticles was determined to be 1.65×10^{-3} mol·g⁻¹ based on inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Various parameters were investigated for the model reaction including catalyst loading, solvent, base, and temperature (Table 1). Different solvents were initially examined. Low yields of the biphenyl compound were observed using H₂O (30%) and EtOH (15%) (Table 1, entries 1 and 2) whereas DMF and DMSO led to the corresponding biphenyl product in 75% and 80% yield respectively (Table 1, entries 4 and 5). Polyethylene glycol (PEG) was selected as the best reaction media in terms of reactivity and activity. Next, the effects of different organic and inorganic bases were examined (Table 1, entries 6-11). The highest yield was achieved using K₂CO₃ (Entry 6). The effect of temperature on the reaction was also examined which showed a gradual increase in yield corresponding with an increase in temperature (Table 1). Based on these results, an optimal temperature of 80 °C was

selected. Finally, the effect of Fe_3O_4/SiO_2 -DTZ-Pd loading was examined. The reaction was performed in the presence of 0.33, 0.50, and 0.66 mol% of Fe_3O_4/SiO_2 -DTZ-Pd (Table 1). Increasing the amount of Fe_3O_4/SiO_2 -DTZ-Pd catalyst to 0.66 mol% did not significantly increase the yield of the biphenyl (Table 1, entry 17). Additionally, the coupling reaction did not occur in the absence of catalyst (Table 1, entry 18). Based on these results the optimum catalyst loading was 0.50 mol%. Likewise, the reaction conditions were optimized for the coupling reaction using phenylboronic acid, (Table 1, entries 19-34). The best result was observed in PEG at 60 °C using 0.33 mol% of catalyst and 3 mmol of Na_2CO_3 as base (Table 1, entry 24).

Table 1. Optimization of the Fe_3O_4/SiO_2 -DTZ-Pd catalyzed Suzuki-Miyaura cross-coupling reaction of iodobenzene with sodium tetraphenylborate or phenylboronic acid.^a

Fe₃O₄/SiO₂-DTZ-Pd

	+ NaPh4	Solvent, base						
Entry	Phenylating	Solvent	Base	Temp.	Cat.	Time	Yield	
1	N-D-D	EtOIL	V.CO	(0)	(mg)	(mm)	(%)	
1	NaPii4D	LICH	K ₂ CO ₃	80	2	20	25	
2	NaPit4D	H ₂ U	K_2CO_3	80	2	20	50	
3	NaPh4D	DMSO	K_2CO_3	80	2	20	15	
5	NaPh ₄ D	DMSO	K_2CO_3	80	2	20	80 75	
5	NaPh ₄ D	DMF	K_2CO_3	80	3	30	06	
7	NaDh D	DEC	K ₂ CO ₃ Et N	80	2	20	90 65	
0	NaPh4D	PEG		80	2	20	80	
ô	NaPh4D	PEG	KOH	80	2	20	80 55	
10	NaPh B	PEG	NaHCO	80	3	30	35	
10	NaPh B	PEG	Narico ₃	80	3	5 h	55	
12	NaPh B	PEG	- K.CO.	80 r t	3	5 h	-	
12	NaPh B	PEG	K_2CO_3	60	3	5 h	20	
13	NaPh B	PEG	K_2CO_3	100	3	35	20	
15	NaPh B	PEG	K_2CO_3	80	2	150	70	
16	NaPh B	PEG	K_2CO_3 K_2CO_3	80	4	35	08	
17	NaPh B	PEG	K ₂ CO ₃	80	-	24 h	-	
19	PhR(OU).	EtOH	N_2CO_3	60	2	130	66	
10	$PhB(OH)_2$	DMSO	Na ₂ CO ₃	60	2	130	57	
20	$PhB(OH)_2$	DMSO	Na_2CO_3	60	2	130	01	
20	$PhB(OH)_2$	PEG	Na_2CO_3 Na_2CO_3	60	2	130	91	
21	$PhB(OH)_2$	PEG	Et.N	60	2	130	55	
22	$PhB(OH)_2$	PEG	Na.CO.	60	2	130	04	
23	$PhB(OH)_2$	PEG	KaCOa	60	2	130	01	
25	$PhB(OH)_2$	PEG	NaHCO ₂	60	2	130	62	
26	PhB(OH)	PEG	-	60	2	130		
27	PhB(OH) ₂	PEG	NacOa	rt	2	5 h	10	
28	$PhB(OH)_2$	PEG	Na ₂ CO ₂	60	2	130	93	
20	$PhB(OH)_2$	PEG	Na ₂ CO ₂	70	2	130	92	
30	$PhB(OH)_2$	PEG	Na ₂ CO ₂	80	2	130	94	
31	PhB(OH)	PEG	Na ₂ CO ₂	60	3	135	95	
32	PhB(OH)	PEG	Na ₂ CO ₂	60	4	130	95	
33	PhB(OH) ₂	PEG	NacOa	60	5	130	97	
^a Peacti	on conditioner i	iadahanzana (1	mmal) M	Dh P (0.5	mmol) (m DhD(OI	D (12	

^a Reaction conditions: iodobenzene (1 mmol), NaPh₄B (0.5 mmol) or PhB(OH)₂ (1.2 mmol), base (3 mmol), solvent (2 mL).

^b Isolated yield (based on the aryl halide).

To explore the generality and scope of the catalytic system, the coupling of various aryl halides (chlorides, bromides and iodides) with sodium tetraphenylborate or phenylboronic acid was examined (Table 2). Aryl halides with both electron withdrawing and donating groups efficiently reacted with sodium tetraphenylborate or phenylboronic acid in the presence of catalytic Fe₃O₄/SiO₂-DTZ-Pd in good to high yields. Interestingly, the reactions were clean and no by-products were detected.

The recyclability of the Fe_3O_4/SiO_2 -DTZ-Pd was also studied. After completion, the catalyst was removed from the reaction mixture by magnetic decantation and subjected to the next catalytic run under the same reaction conditions. The catalyst could be reused at least five times without significant loss of catalytic activity (Figure 1).

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Figure 1. Catalyst recyclability for the reaction of iodobenzene with sodium tetraphenylborate

Conclusion

In conclusion we have developed a simple, clean and efficient synthesis of a MNPs supported-Pd complex and examined its catalytic activity for the synthesis of various biphenyls *via* the reaction of sodium tetraphenylborate or phenylboronic acid with various aryl halides. Mild reaction conditions, low catalyst loading, good to high yields, ease of catalyst separation using an external magnet and simple work-up procedure are some of the attractive features of this protocol. Further studies on the effects of Fe₃O₄/SiO₂-DTZ- Pd catalyst for other systems are in progress in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://www.sciencedirect.com/science/journal/00404039.

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		+ NaPh ₄ B or PhB(OH) ₂	Fe ₃ O ₄ /Si K ₂ CO ₃ or	iO ₂ -DTZ-Pd ► 〈 Na₂CO₃, PEG R´			
Entry	Aryl halide	Phenylating reagent	Time (min)	Yield ^b (%)	m.p. (°C)	TON	TOF (h ⁻¹)
1		NaPh ₄ B	30	98	67-68 ²⁰	198.0	396.0
2		NaPh₄B	35	95	Oil ²¹	191.9	329.0
3	H3C-	NaPh ₄ B	40	95	44-47 ²⁰	191.9	287.9
4	MeO-	NaPh ₄ B	25	97	84-85 ²⁰	196.0	470.4
5		NaPh ₄ B	60	97	Oil ²⁰	196.0	196.0
6	H ₃ C-Br	NaPh ₄ B	20	96	44-47 ²¹	193.9	581.7
7	Br-CI	NaPh ₄ B	60	93	70-71 ²⁰	187.9	187.9
8	Br	NaPh ₄ B	25	92	67-68 ²³	185.9	446.2
9	NCBr	NaPh ₄ B	30	97	82-83 ²³	196.0	392.0
10	OHCBr	NaPh ₄ B	80	96	56-58 ²²	193.9	145.4
11	HO-Br	NaPh ₄ B	50	95	162-163 ²³	191.9	230.3
12	HSBr	NaPh ₄ B	25	93	105-106 ²⁴	187.9	451.1
13	O ₂ N-Br	NaPh ₄ B	30	98	113-115 ²⁰	198.0	396.0
14	H ₂ NBr	NaPh ₄ B	60	95	52-54 ²²	191.9	191.9
15	Br	NaPh₄B	10h	68	Oil ²³	137.3	13.7
16	Č)–cı	NaPh ₄ B	4h	92	66-68 ²⁰	185.9	46.5
17		PhB(OH) ₂	130	94	67-68 ²⁰	284.8	131.4
18	H ₃ C-	PhB(OH) ₂	40	91	44-47 ²⁰	275.8	413.7
19	H ₃ CBr	PhB(OH) ₂	120	89	44-47 ²⁰	269.7	134.9
20	BrCI	PhB(OH) ₂	60	93	70-71 ²⁰	281.8	281.8
21	Br	PhB(OH) ₂	190	90	67-68 ²⁰	272.7	86.1
22	NCBr	PhB(OH) ₂	150	90	82-83 ²³	272.7	109.1
23	HOBr	PhB(OH) ₂	60	92	162-163 ²³	278.8	278.8

Table 2. Suzuki cross-coupling reaction of various aryl halides with sodium tetraphenylborate or phenylboronic acid^a. $\stackrel{\times}{X}$

⁴ Reaction conditions: aryl halide (1 mmol), NaPh₄B (0.5 mmol) or PhB(OH)₂ (1.2 mmol), base (3 mmol), 3 mg (0.5 mol%) of Fe₃O₄/SiO₂-DTZ-Pd for NaPh₄B and 2 mg (0.33 mol%) of Fe₃O₄/SiO₂-DTZ-Pd for PhB(OH)₂, PEG (2 mL). ^b Isolated yield (based on the aryl halide).

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Highlights

Fe₃O₄/SiO₂-DTZ-Pd was prepared

Fe₃O₄/SiO₂-DTZ-Pd was characterized

Acceleration