

Heterogeneous Suzuki reaction catalyzed by MCM-41-supported sulfur palladium(0) complex

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Abstract

The MCM-41-supported sulfur palladium(0) complex has been synthesized from 3-(2-cyanoethylsulfanyl)propyltriethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride, and then the reduction with hydrazine hydrate. The complex has been characterized by powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) and it is a highly active catalyst for the heterogeneous Suzuki reaction affording a variety of biaryls in high to excellent isolated yields. Our system not only solves the basic problems of catalyst separation and recovery but also avoids the use of phosphine ligands.

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1. Introduction

The Suzuki reaction is proving to be increasingly popular method for forming carbon–carbon and has found wide application in organic synthesis [1–4]. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity [1,2]. For Suzuki reactions homogeneous palladium complexes such as Pd(PPh₃)₄ are usually used as the catalysts and the amount of catalyst used is about 1 mol% of reactant. Although homogeneous palladium catalysts have proven to be efficient, it is difficult to recover them from products and use of homogeneous palladium catalysts is still uneconomic for large-scale preparation. From the standpoint of environmentally benign organic synthesis, development of immobilized palladium catalysts is challenging and important [5–7]. In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used infinitely, and contamination of products by palladium is prevented. Although a great deal of effort has been made to carry out such ideal reactions using immobilized palladium catalysts, what seems to be lacking is

the efficiency of the catalytic systems. It is obvious that the heterogeneous catalytic systems exhibit generally lower activity than the homogeneous ones. Recently palladium immobilized on the surface of silica gel [8–11] and an assembled complex of palladium and non-cross-linked amphiphilic polymer [12] have been used for Suzuki reaction. Keeping in view the application and interest of heterogeneous palladium catalysts in academia and industry, there is a need to design and develop highly active, re-usable and easily recoverable chemically supported heterogeneous palladium catalysts.

Our approach was guided by three imperatives: the polymeric ligand should be easily accessible (1), starting from readily available and cheap reagents (2). The polymeric palladium catalyst should be air stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life (3). Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [13]. MCM-41 has a regular pore diameter of ca. 50 Å and a specific surface area >700 m² g⁻¹ [14]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [15–17]. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions [18–22]. However, to the best of our knowledge, there has been no general study of

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Suzuki reaction catalyzed by a MCM-41-supported sulfur palladium complex catalyst described to date. In this paper, we wish to report the synthesis of the first MCM-41-supported sulfur palladium(0) complex [abbreviated as MCM-41-S-Pd(0)] and its catalytic properties in the Suzuki reaction.

2. Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 [23] and 3-(2-cyanoethylsulfanyl)propyltriethoxysilane [24] were easily prepared from commercially available and cheap materials according to literature procedures. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in CDCl_3 as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in CDCl_3 as solvent. X-ray powder diffraction was obtained on Damx-rA (Rigaku). X-ray photoelectron spectra (XPS) were recorded on XSAM 800 (Kratos).

2.1. Preparation of MCM-41-S

A solution of 3-(2-cyanoethylsulfanyl)propyltriethoxysilane (1.55 g, 5.3 mmol) in dry chloroform (18 ml) was added to a suspension of the mesoporous support MCM-41 (3.20 g) in dry toluene (180 ml). The mixture was stirred for 24 h at 100°C . Then the solid was filtered and washed by CHCl_3 (3×20 ml), and dried in vacuum at 160°C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (4.43 g, 40.8 mmol) in dry toluene (130 ml) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3×20 ml) and diethyl ether (3×20 ml), and dried in vacuum at 160°C for 5 h to obtain 3.81 g of hybrid material MCM-41-S. The sulfur content was found to be 0.87 mmol/g by elemental analysis.

2.2. Preparation of MCM-41-S-Pd(0) complex

To a solution of PdCl_2 (0.22 g, 1.3 mmol) in acetone (75 ml) was added the MCM-41-S (3.20 g). The mixture was refluxed for 72 h. The product was allowed to cool, then filtered. The yellow solid was washed with distilled water (3×30 ml) and acetone (3×30 ml), then stirred with hydrazine hydrate (2.3 g) and EtOH (30 ml) at 30°C for 3 h. The resulting product was filtered, washed with EtOH (3×25 ml) and Et_2O (3×25 ml) and dried under vacuum at 60°C to give 3.15 g of the dark gray polymeric palladium(0) complex [MCM-41-S-Pd(0)]. The sulfur and palladium content was 0.72 and 0.35 mmol/g, respectively.

2.3. General procedure for Suzuki coupling of aryl halides with arylboronic acids

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), potassium carbonate (2.0 mmol), DMF (2.5 ml) and the MCM-41-S-Pd(0) complex (0.005 mmol of Pd) was stirred under Ar in an oil bath at 80 – 100°C for 6–24 h. The mixture was cooled and filtered. The MCM-41-S-Pd(0) complex was washed

with distilled water (2×10 ml), DMF (2×10 ml) and Et_2O (2×10 ml) and reused in the next run. The filtrate was poured into a saturated aqueous NaCl solution (50 ml) and extracted with methylene chloride (2×50 ml). The extracts was washed with water (3×30 ml) and dried over MgSO_4 . After removal of the solvent, the residue was purified by column chromatography on silica gel.

3. Results and discussion

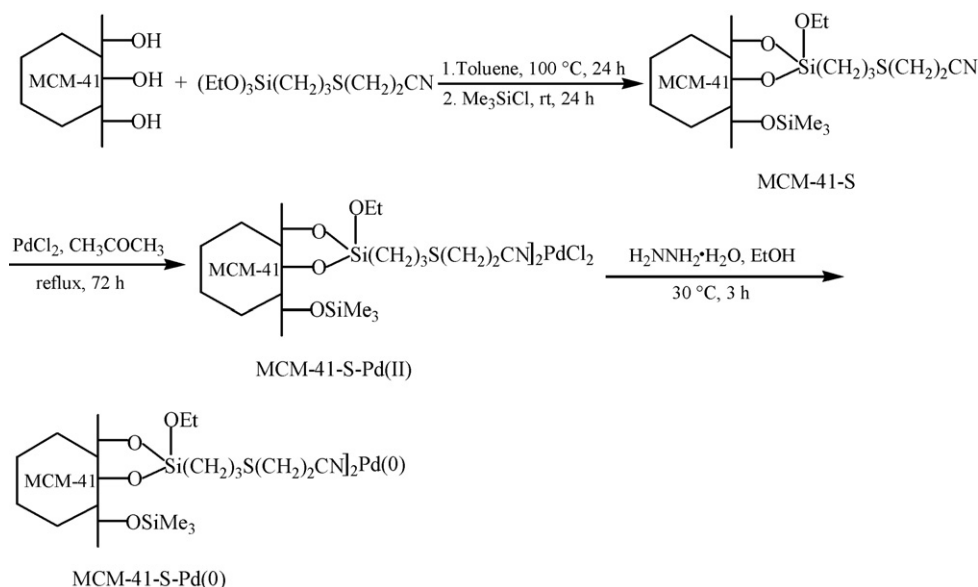
It is well known that zero-valent palladium complexes show unique reactivity in various organic reactions. However, it is very difficult to use the Pd(0) complexes as practical catalysts because of their instability to air and moisture. The first MCM-41-supported sulfur palladium(0) complex was conveniently synthesized from 3-(2-cyanoethylsulfanyl)propyltriethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride in acetone, and then the reduction with hydrazine hydrate in ethanol (Scheme 1).

The X-ray powder diffraction (XRD) analysis of the MCM-41-S-Pd(0) indicated that, in addition to an intense diffraction peak (1 0 0), two higher order peaks (1 1 0) and (2 0 0) with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the MCM-41-supported sulfur palladium(0) complex. The S:Pd mole ratio of the MCM-41-S-Pd(0) was determined to be 2.05. The XPS data for MCM-41-S, MCM-41-S-Pd(II), MCM-41-S-Pd(0) and PdCl_2 are listed in Table 1. It can be seen that the binding energies of Si 2p, N 1s and O 1s of MCM-41-S-Pd(II) are similar to those of MCM-41-S, and the binding energy of Cl 2p of MCM-41-S-Pd(II) is similar to that of PdCl_2 . However, the difference of Pd $3d_{5/2}$ binding energies between MCM-41-S-Pd(II) and PdCl_2 is 0.8 eV. The difference of S 2p binding energies between MCM-41-S-Pd(II) and MCM-41-S is 0.5 eV. These results suggest that a coordination bond between S and Pd is formed in the MCM-41-S-Pd(II). The binding energy (336.7 eV) of Pd $3d_{5/2}$ of MCM-41-S-Pd(0) was lower than the binding energy (337.5 eV) of Pd $3d_{5/2}$ of MCM-41-S-Pd(II). The Pd $3d_{5/2}$ binding energy depends strongly on the nature of the ligands. Consequently, it is impossible to identify the reduced complex as a zerovalent one on the basis of its Pd $3d_{5/2}$ binding energy only. However, the binding energy of Cl 2p in the MCM-41-S-Pd(0) cannot be detected, the shift (lower) of Pd $3d_{5/2}$ binding energy together with the dark gray color suggests that the reduction of the starting

Table 1
XPS data for MCM-41-S, MCM-41-S-Pd(II), MCM-41-S-Pd(0) and PdCl_2^a

Sample	Pd $3d_{5/2}$	S 2p	N 1s	Si 2p	O 1s	Cl 2p
MCM-41-S-Pd(0)	336.7	164.3	400.5	103.2	532.9	
MCM-41-S-Pd(II)	337.5	164.2	399.8	103.3	533.1	199.3
MCM-41-S		163.7	399.7	103.2	533.0	
PdCl_2	338.3					199.2

^a The binding energies are referenced to C 1s (284.6 eV) and the energy differences were determined with an accuracy of ± 0.2 eV.



Scheme 1. Preparation of the MCM-41-S-Pd(0).

palladium(II) complex to the lower valent state has taken place. In addition, the difference of N 1s binding energies between MCM-41-S-Pd(0) and MCM-41-S is 0.8 eV. This result shows that a coordination bond between N and Pd is also formed in the MCM-41-S-Pd(0), which further confirming the reduction of the MCM-41-S-Pd(II) to the MCM-41-S-Pd(0). The MCM-41-S-Pd(0) complex formed is stable in air but for prolonged storage is better stored under an atmosphere of argon in which case no decomposition and deactivation are noted over the period of 6 months at room temperature.

In order to test the catalytic activity of the first MCM-41-supported sulfur palladium(0) complex [MCM-41-S-Pd(0)], the Suzuki reactions of arylboronic acids with aryl halides were studied. The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. The influences of bases, solvents and amounts of the catalyst on catalytic property of the MCM-41-S-Pd(0) complex were investigated by using coupling reaction of iodobenzene with phenylboronic acid. The results are showed in Table 2.

It was found that among the bases tested, anhydrous K_2CO_3 proved to be the most efficient. Among the solvents used, DMF was the best choice. Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of biphenyl (entry 12). Taken together, excellent result was obtained when the coupling reaction was carried out with 0.5 mol% of MCM-41-S-Pd(0) using K_2CO_3 as base in DMF at $80^\circ C$ (entry 8).

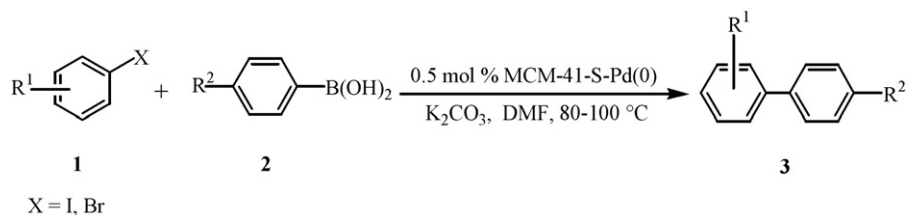
To examine the scope for this coupling reaction, a variety of aryl iodides and bromides were coupled with different phenylboronic acids in DMF in the presence of a catalytic amount of MCM-41-S-Pd(0) using K_2CO_3 as base (Scheme 2). The typical experimental results are summarized in Table 3. As shown in Table 3, the Suzuki coupling reactions of a variety of aryl iodides with arylboronic acids proceeded very smoothly at $80^\circ C$ giving the corresponding coupling products in excellent isolated yields after 6 h. The reactivity of aryl bromides was lower than that of aryl iodides and the coupling reactions required slightly higher temperature and longer times. As seen from Table 3, the

Table 2
Coupling reaction of iodobenzene with phenylboronic acid in the presence of several bases and solvents^a

Entry	Base	Solvent	MCM-41-S-Pd(0) (mol%)	Time (h)	Yield ^b (%)
1	K_3PO_4	<i>o</i> -Xylene	0.5	8	70
2	K_3PO_4	DMF	0.5	8	81
3	K_3PO_4	Dioxane	0.5	8	73
4	Na_2CO_3	<i>o</i> -Xylene	0.5	8	85
5	Na_2CO_3	DMF	0.5	6	93
6	Na_2CO_3	Dioxane	0.5	8	88
7	K_2CO_3	<i>o</i> -Xylene	0.5	8	90
8	K_2CO_3	DMF	0.5	6	98
9	K_2CO_3	Dioxane	0.5	8	92
10	K_2CO_3	DMF	0.3	10	96
11	K_2CO_3	DMF	0.1	24	92
12	K_2CO_3	DMF	1.0	3.5	95

^a All reactions were performed using 1.0 mmol of iodobenzene, 1.5 mmol of phenylboronic acid, 2.0 mmol of base in 2.5 ml of solvent at $80^\circ C$ under Ar.

^b Isolated yield based on the iodobenzene used.



Scheme 2. Suzuki reaction catalyzed by MCM-41-S-Pd(0).

Table 3
Heterogeneous Suzuki reaction of aryl iodides and bromides with arylboronic acids catalyzed by MCM-41-S-Pd(0)^a

Entry	R ¹	X	R ²	Temperature (°C)	Time (h)	Product	Yield (%) ^b
1	H	I	H	80	6	3a	98
2	4-CH ₃ O	I	H	80	6	3b	96
3	4-O ₂ N	I	H	80	6	3c	95
4	4-CH ₃ O	I	4-Cl	80	6	3d	94
5	4-Cl	I	4-Cl	80	6	3e	97
6	3-O ₂ N	I	4-Cl	80	6	3f	96
7	4-CH ₃ OCO	I	4-Cl	80	6	3g	97
8	4-Cl	I	4-CH ₃	80	6	3h	98
9	4-CH ₃ O	I	4-CH ₃	80	6	3i	96
10	4-O ₂ N	I	4-CH ₃	80	6	3j	97
11	H	Br	H	100	10	3a	86
12	4-CHO	Br	H	100	10	3k	90
13	4-CH ₃ OCO	Br	H	100	10	3l	88
14	4-CH ₃ O	Br	4-Cl	100	10	3d	87
15	3-CN	Br	H	100	10	3m	89
16	4-Cl	Br	4-Cl	100	10	3e	90
17	4-Cl	Br	4-CH ₃	100	10	3h	89
18	4-CH ₃ O	Br	4-CH ₃	100	10	3i	88
19	4-O ₂ N	Br	4-CH ₃	100	10	3j	89
20	2-CN	Br	4-CH ₃	100	24	3n	82

^a Reactions were carried out with 1 mmol of aryl halide, 1.5 mmol of arylboronic acid, 0.005 mmol of palladium catalyst, 2 mmol of K₂CO₃ in 2.5 ml of DMF.

^b Yield of isolated product **3** based on the aryl halide.

Suzuki coupling reactions of a variety of aryl bromides with arylboronic acids could also proceed smoothly at 100 °C to afford the corresponding coupling products in high isolated yields on longer times. A favorable effect of electron-withdrawing substituents is normally observed in palladium-catalyzed reactions [25]. With our catalyst, however, electron-withdrawing groups in aryl halides have relatively little effect on the coupling reaction. Substituted chlorobenzenes are inert under the same conditions giving traces of cross-coupling products. To further illustrate that chloroarenes are inert in the reaction system, 4,4'-dichlorobiphenyl was selectively produced in the reaction of (4-chlorophenyl)boronic acid with 1-bromo-4-chlorobenzene (Table 3, entry 16).

This MCM-41-supported sulfur palladium(0) catalyst can be easily recovered by simple filtration. In an attempt to show that the MCM-41-S-Pd(0) can be recycled, the coupling reaction of iodobenzene with phenylboronic acid was repeated 10 times using the same batch of supported catalyst. The isolated yields of biphenyl remain around 97% and turnover numbers of several thousand have been achieved based on 10 filtrations and reuse experiments from batch reactions clearly illustrating the high stability and excellent reusability of the catalyst. The result is important from a practical point of view. A further objective of our studies was to determine whether the catalysis was due to

the MCM-41-S-Pd(0) complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end. To test this, we performed the hot filtration test [26]. We focused on the coupling reaction of 1-bromo-4-chlorobenzene with phenylboronic acid. We filtered off the MCM-41-S-Pd(0) complex after 2 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (100 °C) in order to avoid possible re-coordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed and no palladium could be detected in the liquid reaction mixtures by atomic absorption spectroscopy (AAS). This suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction.

4. Conclusion

We have described the first MCM-41-supported sulfur palladium(0) complex whose preparation is rather simple and convenient. This complex is a highly efficient, stable and recyclable heterogeneous catalyst for the Suzuki coupling reactions of aryl iodides and bromides with arylboronic acids. Our system not only solves the basic problems of catalyst separation and recovery but also avoids the use of phosphine ligands.

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