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Mercapto-Functionalized MCM-41 Anchored Palladium(0) Complex as an Efficient Catalyst for the Heterogeneous Suzuki Reaction

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Abstract Mercapto-functionalized MCM-41 anchored palladium(0) complex is an efficient catalyst for the heterogeneous Suzuki reaction of arylboronic acids with aryl halides. Our system not only solves the basic problems of catalyst separation and recovery but also avoids the use of phosphine ligands.

Keywords Supported palladium catalyst · MCM-41 · Suzuki coupling · Mercapto palladium(0) complex · Heterogeneous catalysis

1 Introduction

The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [1]. The Suzuki reaction is proving to be increasingly popular method for the construction of unsymmetrical biaryl compounds and has found wide applications in organic synthesis [2–4]. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity [2]. It is a homogeneous reaction, generally using soluble palladium complexes such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ as catalysts. The amount of palladium catalyst used is about 2 mol% of reactant; however, use of homogeneous palladium catalysts is still uneconomic for large-scale preparations in the laboratory and for industrial production. 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. Despite the general use of the Suzuki reaction in organic synthesis, polymer-supported palladium catalysts have not been widely used for this reaction yet [8–11]. Study of new types of polymer-supported palladium catalysts which might be suitable for the Suzuki reaction has theoretical and practical significance. In the past, most of these studies have been related to polymer-supported phosphine palladium catalysts [12–14]. It is known that catalysts containing phosphine ligands are unstable [15–17]. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complex is rather complicated since the synthesis of the phosphine ligands requires multi-step sequences. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and good stability is a topic of enormous importance.

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 [18]. MCM-41 has a regular pore diameter of ca.50 Å and a specific surface area > 700 m^2g^{-1}

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[19]. 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 [20–22]. It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions [23–27]. However, to the best of our knowledge, there has been no general study of Suzuki reaction catalyzed by a MCM-41-supported palladium complex catalyst described to date. In this paper, we wish to report the synthesis of the mercapto-functionalized MCM-41 anchored palladium(0) complex [abbreviated as MCM-41-SH-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 [28] was prepared according to literature procedure. X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos). IR spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent.

2.1 Preparation of MCM-41-SH

A solution of γ-mercaptopropyltriethoxysilane (1.70 g, 7.1 mmol) in dry chloroform (12 mL) was added to a suspension of the mesoporous support MCM-41 (2.20 g) in dry toluene (120 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 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 (3.05 g, 28 mmol) in dry toluene (100 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 2.82 g of hybrid material MCM-41-SH. The sulfur content was found to be 0.95 mmol/g by elemental analysis.

2.2 Preparation of MCM-41-SH-Pd(0) Complex

To a solution of $PdCl_2$ (0.154 g, 0.87 mmol) in acetone (50 mL) was added the MCM-41-SH (2.20 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 (1.6 g) and EtOH (25 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 2.07 g of the dark gray mercapto-functionalized MCM-41 anchored palladium(0) complex [MCM-41- SH-Pd(0)]. The sulfur and palladium content was 0.81 and 0.38 mmol/g, respectively.

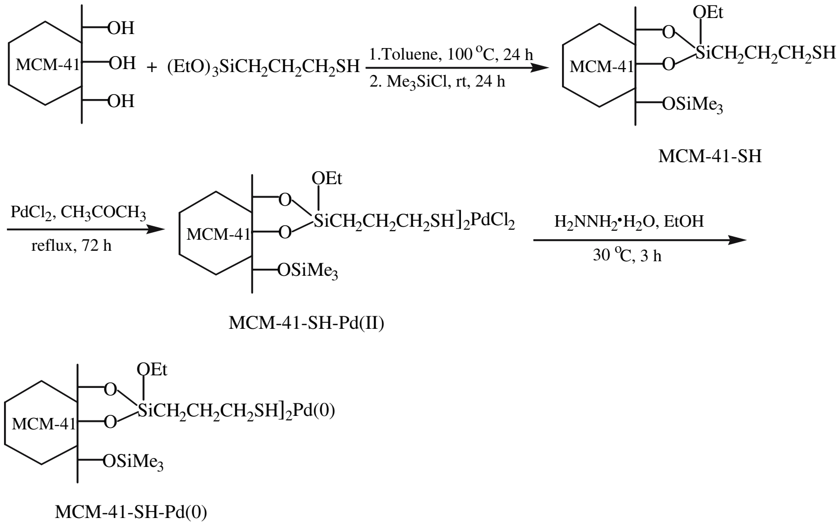
2.3 General Procedure for Suzuki Coupling of Aryl Halides with Arylboronic Acids

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-SH-Pd(0) complex (0.005 mmol of Pd) was stirred under Ar in an oil bath at 80–100 °C for 6–10 h. The mixture was cooled and filtered. The MCM-41-SH-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

The mercapto-functionalized MCM-41 anchored palladium(0) complex [MCM-41- SH-Pd(0)] was conveniently synthesized from commercially available and cheap γ-mercaptopropyltriethoxysilane 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 XRD analysis of the MCM-41-SH-Pd(0) indicated that, in addition to an intense diffraction peak (100), two higher order peaks with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. The nitrogen adsorption studies demonstrated that a significant decrease in pore size by virtue of silylation of the MCM-41 channels was observed. Additionally, upon modification the surface area and pore volume decreased obviously. These results are in good agreement with the fact that the surface modification indeed occurred inside the primary mesopores of the MCM-41.

Scheme 1



Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the mercapto-functionalized MCM-41 anchored palladium(0) complex. The sulfur and palladium content of the MCM-41-SH-Pd(0) was determined to be 0.81 and 0.38 mmol/g, respectively, and the S:Pd mole ratio of this complex was 2.13. The XPS data for MCM-41-SH, MCM-41-SH-Pd(II), MCM-41-SH-Pd(0) and $PdCl_2$ are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-SH-Pd(II) are similar to those of MCM-41-SH, and the binding energy of Cl_{2p} of MCM-41-SH-Pd(II) is similar to that of $PdCl_2$. However, the difference of $Pd_{3d5/2}$ binding energies between MCM-41-SH-Pd(II) and $PdCl_2$ is 0.9 eV. The difference of S_{2p} binding energies between MCM-41-SH-Pd(II) and MCM-41-SH is 0.5 eV. These results suggest that a coordination bond between S and Pd is formed in the MCM-41-SH-Pd(II). The binding energy (336.8 eV) of $Pd_{3d5/2}$ of MCM-41-SH- Pd(0) was lower than the binding energy (337.4 eV) of $Pd_{3d5/2}$ of MCM-41-SH-Pd(II). The $Pd_{3d5/2}$ 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 $Pd_{3d5/2}$ binding energy only. However, the binding energy of Cl_{2p} in the MCM-41-SH-Pd(0) cannot be detected, the shift (lower) of $Pd_{3d5/2}$ binding energy together with the change in color (from yellow to dark gray) suggests that the reduction of the starting palladium(II) complex to the lower valent state has taken place.

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

Sample	$Pd_{3d5/2}$	S_{2p}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-SH-Pd(0)	336.8	164.2	103.2	533.0	
MCM-41-SH-Pd(II)	337.4	164.3	103.3	533.1	199.3
MCM-41-SH		163.8	103.2		
$PdCl_2$	338.3			533.0	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

In order to evaluate the catalytic activity of the mercapto-functionalized MCM-41 anchored palladium(0) complex [MCM-41-SH-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-SH-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 didn't increase the yield of biphenyl (entry 11). Taken together, excellent result was obtained when the coupling reaction was performed with 0.5 mol% of MCM-41-SH-Pd(0) using K_2CO_3 as base in DMF at 80 °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-SH-Pd(0) using K_2CO_3 as base (Scheme 2). The typical experimental results are summarized in Table 3. As shown in Table3, the Suzuki coupling reactions of a variety of aryl iodides with arylboronic acids proceeded very smoothly at 80 °C giving the corresponding coupling products in excellent isolated yields after 6 h. As expected, the reactivity of aryl bromides was lower than that of aryl iodides and the coupling reactions of aryl bromides required slightly higher temperature and longer times. As seen from Table 3, the

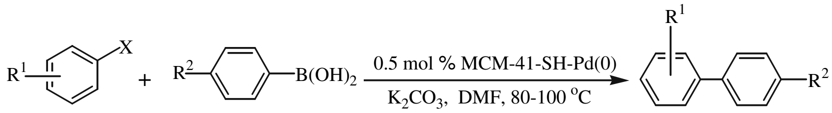
Table 2 Coupling reaction of iodobenzene with phenylboronic acid in the presence of several bases and solvents[a]

Entry	Base	Solvent	MCM-41-SH-Pd(0) (mol%)	Time (h)	Yield[b] (%)
1	K_3PO_4	*o*-Xylene	0.5	9	72
2	K_3PO_4	DMF	0.5	9	79
3	K_3PO_4	Dioxane	0.5	9	70
4	Na_2CO_3	*o*-Xylene	0.5	8	84
5	Na_2CO_3	DMF	0.5	6	92
6	Na_2CO_3	Dioxane	0.5	8	85
7	K_2CO_3	*o*-Xylene	0.5	8	87
8	K_2CO_3	DMF	0.5	6	96
9	K_2CO_3	Dioxane	0.5	8	91
10	K_2CO_3	DMF	0.3	12	95
11	K_2CO_3	DMF	1.0	4	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 °C under Ar

[b] Isolated yield based on the iodobenzene used

Scheme 2



1 2 3

X = I, Br

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

Entry	R^1	X	R^2	Temp (°C)	Time (h)	Product	Yield (%)[b]
1	H	I	H	80	6	**3a**	96
2	4-CH_3	I	H	80	6	**3b**	95
3	4-O_2N	I	H	80	6	**3c**	96
4	4-Cl	I	4-Cl	80	6	**3d**	97
5	4-CH_3O	I	4-Cl	80	6	**3e**	94
6	4-CH_3OCO	I	4-Cl	80	6	**3f**	93
7	3-O_2N	I	4-Cl	80	6	**3g**	95
8	4-O_2N	I	4-CH_3	80	6	**3h**	96
9	4-CH_3O	I	4-CH_3	80	6	**3i**	94
10	4-Cl	I	4-CH_3	80	6	**3j**	95
11	H	Br	H	100	10	**3a**	84
12	4-CHO	Br	H	100	10	**3k**	89
13	4-CH_3OCO	Br	H	100	10	**3l**	86
14	4-CH_3O	Br	4-Cl	100	10	**3e**	88
15	3-CN	Br	H	100	10	**3m**	86
16	4-Cl	Br	4-Cl	100	10	**3d**	87
17	4-Cl	Br	4-CH_3	100	10	**3j**	88
18	4-CH_3O	Br	4-CH_3	100	10	**3i**	85
19	4-O_2N	Br	4-CH_3	100	10	**3h**	87

[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 K_2CO_3 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 [29]. 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 coupling reaction of (4-chlorophenyl)boronic acid with 1-bromo-4-chlorobenzene (Table 3, entry 16).

A further objective of our studies was to determine whether the catalysis was due to the MCM-41-SH-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 [30]. We focused on the coupling reaction of 1-bromo-4-chlorobenzene with (4-chlorophenyl)boronic acid. We filtered off the MCM-41-SH-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 recoordination 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.

This mercapto-functionalized MCM-41 anchored palladium(0) complex catalyst can be easily recovered by simple filtration. In an attempt to show that the MCM-41-SH-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 94% 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. The possible reasons without palladium leaching from the MCM-41-SH-Pd(0) catalyst may be: (1) the heterogeneous MCM-41-SH-Pd(0) catalyst was a highly stable sulfur palladium complex due to the strong complexing action of the mercapto ligand on palladium, (2) the catalytic palladium species was anchored on the inner surface of the mesopore of MCM-41 support, so there was no strong complexing and solvolytic action of the solvent.

4 Conclusion

We have prepared the novel mercapto-functionalized MCM-41 anchored palladium(0) complex [MCM-41-SH-Pd(0)] from γ-mercaptopropyltriethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride, and then the reduction with hydrazine hydrate. It was found that the novel phosphine-free heterogeneous palladium complex [MCM-41-SH-Pd(0)] is a highly efficient, stable and recyclable catalyst for the Suzuki reactions of arylboronic acids with aryl halides. The advantages of our heterogeneous catalytic system over others are: (1) the preparation of the heterogeneous MCM-41-SH-Pd(0) catalyst is very simple and convenient from commercially available and cheap reagents, (2) excellent performance and reusability of the catalyst.

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