

The first MCM-41-supported thioether palladium(0) complex: A highly active and stereoselective catalyst for Heck arylation of olefins with aryl halides

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Abstract

The first MCM-41-supported thioether 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. It was found that this complex has not only high activity and stereoselectivity for arylation reaction of conjugated alkenes with aryl iodides or activated aryl bromides, but also can efficiently catalyze the arylation reaction of conjugated alkenes with unactivated bromoarenes. This polymeric palladium catalyst can be easily recovered from the products and reused at least 10 times without loss of activity.

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1. Introduction

The palladium(0)-catalyzed reaction of aryl and alkenyl halides with olefins (the Heck reaction) represents one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications [1]. The Heck reaction is generally catalyzed by soluble palladium complexes with phosphine ligands. However, the reaction suffers from severe problems related with the separation, recovery and instability of the homogeneous catalysts at high temperature, which have so far precluded its widespread industrial applications. These problems can be overcome, however, by the use of heterogeneous catalysts, made up of supported palladium complexes. Supported metal complexes having high activity and selectivity are currently attracting great interest because they can be easily separated and recovered [2]. Although a number of supported palladium catalysts were reported to be effective for Heck reaction [3], very few catalysts were shown to have good catalytic activity for Heck arylation of olefins with unactivated bromoarenes [4]. Among these reported supported palladium

catalysts, most of them are the supported phosphine palladium complexes which suffer from severe disadvantages that have so far precluded their practical applications. It is known that catalysts containing phosphine ligands are unstable at high temperature [5]. Furthermore, the procedure for preparing the polymer-bound phosphine palladium complex is rather complicated; the non-crosslinked poly(chloromethylstyrene) is not commercially available, and the chloromethylation requires the use of carcinogenic chloromethyl methyl ether. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and stability is a topic of enormous importance.

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [6]. MCM-41 has a regular pore diameter of *ca.* 50 Å and a specific surface area >700 m² g⁻¹ [7]. 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 [8]. In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by silica gel. However, to the best of our knowledge, there has been no general study of Heck arylation reactions of olefins with aryl halides catalyzed by a MCM-41-supported thioether palladium(0) complex described to date. In

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this paper, we want to report the preparation of the first MCM-41-supported thioether palladium(0) complex [abbreviated as MCM-41-S-Pd(0)] and its catalytic behavior in the Heck arylation of olefins with aryl halides.

2. Results and discussion

2.1. Preparation of the first MCM-41-supported thioether palladium(0) complex

The mesoporous material MCM-41 was easily prepared from tetramethoxysilane (TMOS) and cetyltrimethylammonium bromide (CTAB) according to literature procedure [9]. The first MCM-41-supported thioether palladium(0) complex [MCM-41-S-Pd(0)] was prepared from 3-(2-cyanoethylsulfanyl)propyltriethoxysilane [10] via immobilization on MCM-41, followed by reacting with palladium chloride in acetone, and then the reduction with hydrazine hydrate in ethanol (Fig. 1).

Fig. 2 shows the XRD patterns for the parent MCM-41 and the modified materials MCM-41-S and MCM-41-S-Pd(0). The parent MCM-41 is a well-ordered mesoporous phase which can be indexed according to a hexagonal lattice characteristic of MCM-41 [6,7]. For MCM-41-S and MCM-41-S-Pd(0), the (1 0 0) reflection of the parent MCM-41 with decreased intensity was remained after functionalization, while the (1 1 0) and (2 0 0) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the MCM-41-supported thioether 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

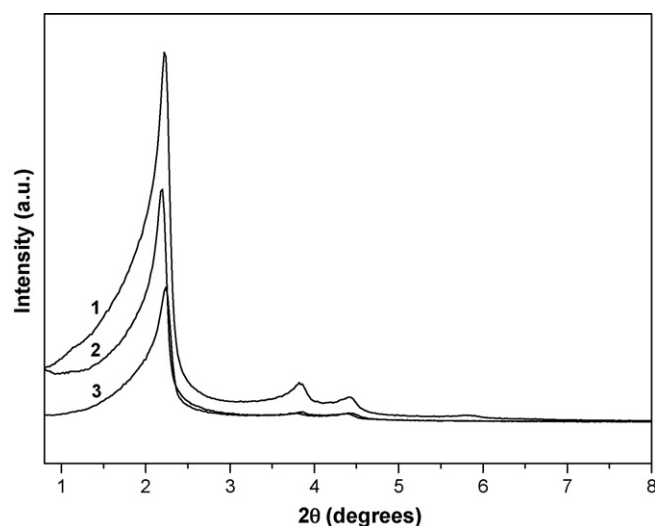


Fig. 2. XRD patterns of catalytic materials: (1) MCM-41; (2) MCM-41-S; (3) MCM-41-S-Pd(0).

Table 1

XPS data for MCM-41-S, MCM-41-S-Pd(II), MCM-41-S-Pd(0) and PdCl₂^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.

MCM-41-S, MCM-41-S-Pd(II), MCM-41-S-Pd(0) and PdCl₂ 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 PdCl₂. However, the difference of Pd 3d_{5/2} binding energies between MCM-41-S-Pd(II) and

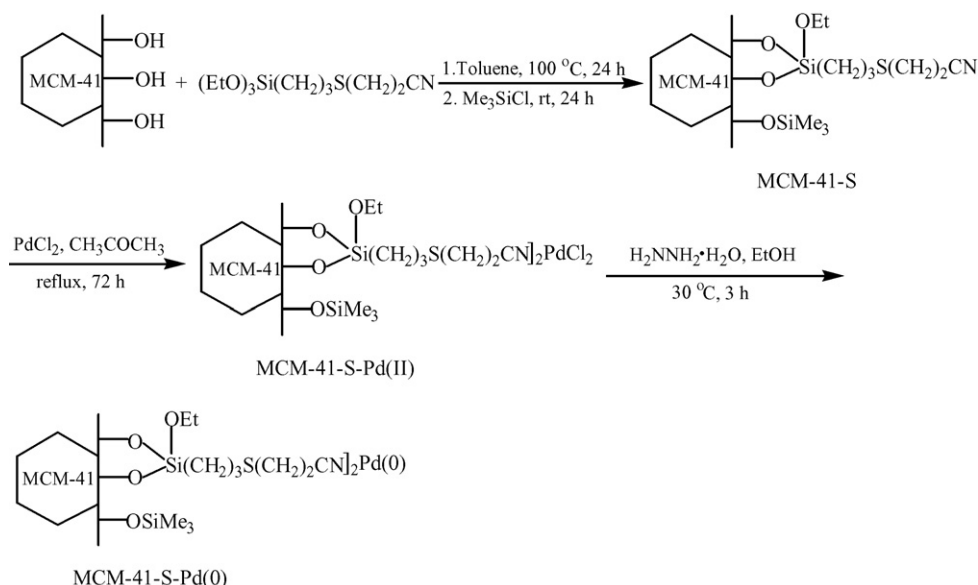


Fig. 1. Preparation of MCM-41-S-Pd(0).

Table 2
Heck arylation of styrene with iodobenzene in the presence of several bases and solvents^a

Entry	Base	Solvent	MCM-41-S-Pd(0) (mol%)	Temperature (°C)	Time (h)	Yield ^b of <i>trans</i> -stilbene (%)
1	Et ₃ N	<i>p</i> -Xylene	0.3	90	6	81
2	Et ₃ N	DMF	0.3	90	6	85
3	Et ₃ N	NMP	0.3	90	6	88
4	Bu ₃ N	<i>p</i> -Xylene	0.3	100	6	89
5	Bu ₃ N	DMF	0.3	100	6	93
6	Bu ₃ N	NMP	0.3	100	6	98
7	NaOAc	DMF	0.3	100	6	84
8	NaOAc	NMP	0.3	100	6	87
9	Bu ₃ N	NMP	0.6	100	4	96
10	Bu ₃ N	NMP	0.1	100	10	94
11	Bu ₃ N	NMP	0.05	100	24	91

^a All reactions were performed using 5.0 mmol of iodobenzene, 5.5 mmol of styrene and 6.0 mmol of base in 2 ml of solvent.

^b Isolated yield based on the iodobenzene used.

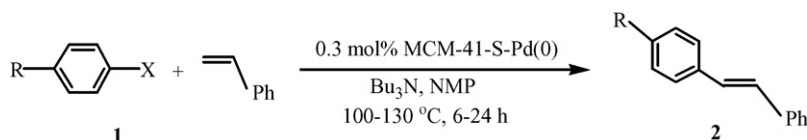
PdCl₂ is 0.8 eV. The difference of S 2p binding energies between MCM-41-S-Pd(II) and MCM-41-S is 0.5 eV. These results suggest that a coordination bond between S and Pd is formed in the MCM-41-S-Pd(II). The binding energy (336.7 eV) of Pd 3d_{5/2} of MCM-41-S-Pd(0) was lower than the binding energy (337.5 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 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.

2.2. Use of MCM-41-S-Pd(0) as a catalyst for arylation of styrene with aryl halides

Synthesis of *trans*-stilbenes assumes importance because of their large molecular hyperpolarizable property suited for the construction of non-linear optics [11] and their uses as organic intermediates [12]. Synthesis of *trans*-stilbenes usually involves a tedious multistep synthetic procedure and the yields are poor to moderate. An arylation of styrene with aryl halides attempted by Heck using palladium salts as catalyst afforded moderate yields on longer reaction time [1a]. Anderson and coworkers [3b] indi-

cated that polymeric palladium catalysts tend to be more efficient in the Heck reaction. Heterogeneous catalysis, however, was performed almost entirely with aryl iodides or electron-deficient aryl bromides. The influences of bases, solvents and amount of the catalyst on catalytic property of MCM-41-S-Pd(0) complex were investigated by using Heck arylation reaction of styrene with iodobenzene. The results are summarized in Table 2. It can be seen from Table 2 that while Et₃N and NaOAc could be used as the base with good results, Bu₃N appeared to be superior. Among these selected solvents such as *p*-xylene, DMF and NMP, the NMP was found to be the best one. *trans*-stilbene was obtained in 98% yield when the Heck arylation reaction was conducted at 100 °C for 6 h using 0.3 mol% of MCM-41-S-Pd(0) complex and Bu₃N as base in NMP (entry 6). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of *trans*-stilbene (entry 9). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental results (entries 10 and 11). We found that, in the presence of a catalytic amount of the MCM-41-S-Pd(0) complex, the arylation reaction of styrene with a variety of aryl iodides or bromides proceeded smoothly in NMP at 100–130 °C using tributylamine as base giving the corresponding *trans*-stilbenes in high yields. The *trans*-selectivity was always near quantitative and no *cis*-product was observed (Scheme 1). The results are summarized in Table 3.

As seen from Table 3, the arylation reaction of styrene with aryl iodides proceeded very smoothly at 100 °C using MCM-41-S-Pd(0) complex as catalyst to give the desired *trans*-products in excellent yields. The substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides and the reactivity of aryl bromides with electron-withdrawing substituents was higher than that of aryl bromides with electron-donating substituents. The arylation reaction of styrene with aryl bromides with electron-withdrawing substituents could pro-



Scheme 1.

Table 3
Heck arylation reaction of styrene with aryl halides^a

Entry	R	X	Temperature (°C)	Time (h)	Product	Yield ^b (%)
1	H	I	100	6	2a	98
2	Cl	I	100	6	2b	97
3	CH ₃ O	I	100	6	2c	98
4	O ₂ N	I	100	6	2d	99
5	CH ₃	I	100	6	2e	96
6	H ^c	Br	130	18	2a	81
7	Cl	Br	130	12	2b	88
8	CH ₃ O ^c	Br	130	24	2c	78
9	CH ₃ ^c	Br	130	24	2e	80
10	O ₂ N	Br	130	12	2d	91
11	CH ₃ OCO	Br	130	12	2f	89
12	OHC	Br	130	12	2g	87

^a Using 5 mmol of aryl halide, 5.5 mmol of styrene, 6 mmol of Bu₃N, and MCM-41-S-Pd(0) (0.015 mmol of Pd) in 2 ml of *N*-methylpyrrolidone (NMP).

^b Isolated yield based on the aryl halide **1** used.

^c 0.3 mol% PPh₃ was added.

ceed smoothly at 130 °C using MCM-41-S-Pd(0) complex as catalyst to afford the corresponding *trans*-stilbenes in high yields (entries 7, 10–12), but the arylation reaction of styrene with bromobenzene or aryl bromides having electron-donating substituents under the same conditions was very slow. However, in the presence of a catalytic amounts of MCM-41-S-Pd(0) complex and PPh₃, the arylation reaction of styrene with bromobenzene or aryl bromides having electron-donating substituents could also take place at 130 °C and the desired *trans*-products were obtained in good yields on longer reaction time (entries 6, 8 and 9). In all reactions only 0.3 mol% catalyst based on the aryl halides was used. As for the arylation reaction of styrene with iodobenzene, the mole turnover numbers of 327 are much larger than those of 75 in the corresponding homogeneous reaction reported by Heck and Nolley [13]. Heck arylation reaction of styrene with iodobenzene with 1 mol% Pd(OAc)₂ in the presence of 2 mol% PPh₃ was performed in NMP at 100 °C using Bu₃N as base to compare with the supported catalyst. It was found that *trans*-stilbene was obtained in 85% isolated yield after 12 h of reaction time and the lower mole turnover numbers of 85 was achieved, and the palladium black was formed in the product. In order to compare with the MCM-41-S-Pd(0) catalyst, the model homogeneous Heck reaction of styrene with iodobenzene with 1 mol% PdCl₂ in the presence of 2 mol% BuSCH₂CH₂CN ligand was also carried out in NMP at 100 °C using Bu₃N as base, *trans*-stilbene was obtained in 89% isolated yield after 8 h of reaction time and the palladium black was also observed after the reaction. However, with our catalytic system, no sign of pal-

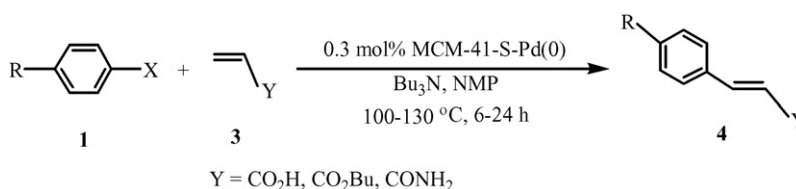
ladium particle formation was observed during/after the reaction.

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 focused on the arylation reaction of styrene with 1-bromo-4-chlorobenzene. We filtered off the MCM-41-S-Pd(0) complex after 1 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (130 °C) in order to avoid possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, little further reaction was observed. This suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction.

2.3. Use of MCM-41-S-Pd(0) as a catalyst for arylation of acrylic acid and its derivatives with aryl halides

We have also investigated the catalytic characteristics of the novel polymeric sulfur palladium catalyst in Heck arylation of other conjugated alkenes with aryl halides (Scheme 2). Cinnamic acids are important chemical substances and organic intermediates and usually prepared by Perkin reaction; however, the yields and stereoselectivity are poor to moderate [14]. Heck arylation reaction of acrylic acid with aryl halides catalyzed by the supported palladium catalysts has received less attention [3d]. We found that, in the presence of a catalytic amount of the MCM-41-S-Pd(0) complex, the arylation reaction of acrylic acid with aryl iodides or aryl bromides having electron-withdrawing substituents proceeded smoothly in NMP at 100–130 °C using tributylamine as base giving the corresponding *trans*-cinnamic acids in high to excellent yields. The arylation reaction of acrylic acid with bromobenzene or aryl bromides having electron-donating substituents under the same conditions proceeded very slowly. To the best of our knowledge, no successful arylation of acrylic acid with unactivated bromoarenes catalyzed by a supported palladium catalyst has been reported. However, in the presence of a catalytic amounts of MCM-41-S-Pd(0) complex and PPh₃, the arylation reaction of acrylic acid with unactivated bromoarenes could also proceed smoothly at 130 °C to give the corresponding *trans*-cinnamic acids in good yields on longer reaction time. The results are summarized in Table 4.

Cinnamates are important synthetic intermediates and usually prepared by utilizing a Wittig type approach [15]. The palladium catalyzed arylation reaction of acrylates with aryl halides



Scheme 2.

Table 4
Heck arylation of acrylic acid and its derivatives with aryl halides^a

R	X	Y	Temperature (°C)	Time (h)	Product	Yield ^b (%)
H	I	CO ₂ H	100	6	4a	97
O ₂ N	I	CO ₂ H	100	6	4b	98
CH ₃ O	I	CO ₂ H	100	6	4c	96
H ^c	Br	CO ₂ H	130	16	4a	83
CH ₃ OCO	Br	CO ₂ H	130	12	4d	92
CH ₃ O ^c	Br	CO ₂ H	130	24	4c	78
CH ₃ ^c	Br	CO ₂ H	130	24	4e	80
H	I	CO ₂ Bu	100	6	4f	97
CH ₃ O	I	CO ₂ Bu	100	6	4g	98
H ^c	Br	CO ₂ Bu	130	18	4f	85
CH ₃ O ^c	Br	CO ₂ Bu	130	24	4g	81
Cl	Br	CO ₂ Bu	130	12	4h	89
H	I	CONH ₂	100	6	4i	94
O ₂ N	I	CONH ₂	130	12	4j	96
O ₂ N	Br	CONH ₂	130	12	4j	87
CH ₃ ^c	Br	CONH ₂	130	24	4k	80
CH ₃ O ^c	Br	CONH ₂	130	24	4l	77

^a Using 5 mmol of aryl halide, 5.5 mmol of **3**, 6 mmol of Bu₃N, and MCM-41-S-Pd(0) (0.015 mmol of Pd) in 2 ml of *N*-methylpyrrolidone (NMP). 11 mmol of Bu₃N was required for acrylic acid.

^b Isolated yield based on the aryl halide **1** used.

^c 0.3 mol% PPh₃ was added.

or arenesulphonyl chlorides has provided a direct route to stereoselective synthesis of *trans*-cinnamates [16], but the homogeneous palladium catalysts cannot be recovered and reused. As shown in Table 4, the arylation reaction of butyl acrylate with aryl iodides or activated aryl bromides proceeded smoothly in NMP at 100–130 °C using MCM-41-S-Pd(0) complex as catalyst and tributylamine as base to afford the desired *trans*-butyl cinnamates in high to excellent yields. Although the reactivity of unactivated aryl bromides was low under the same conditions, the arylation reaction could also take place at 130 °C in the presence of a catalytic amount of PPh₃ giving the corresponding *trans*-butyl cinnamates in good yields. Cinnamamides are also important synthetic intermediates [17]. Zhang et al. reported a polymer-supported phenanthroline palladium(0) catalyzed arylation of acrylamide with aryl iodides, however, this polymeric palladium catalyst did not catalyze the reaction of acrylamide with aryl bromides [17b]. In the presence of tributylamine and a catalytic amount of MCM-41-S-Pd(0) complex, a variety of substituted *trans*-cinnamamides were synthesized from acrylamide and aryl iodides or activated aryl bromides in high yields. To the best of our knowledge, there has been no general study of Heck arylation reaction of acrylamide and unactivated bromoarenes with a supported palladium catalyst described to date. In our study, we found that, in the presence of a catalytic amounts of MCM-41-S-Pd(0) complex and PPh₃, the arylation reaction of acrylamide with unactivated bromoarenes proceeded smoothly in NMP at 130 °C using tributylamine as base giving the corresponding *trans*-cinnamamides in good yields on longer reaction time. The typical results are also summarized in Table 4. Table 4 shows that the nature of the substituents in aryl iodides did not exert significant effect on the yields in all reactions.

2.4. Catalyst recycling

In an attempt to show that the MCM-41-S-Pd(0) complex can be recycled, the arylation reaction of styrene with iodobenzene was repeated 10 times using the same batch of supported catalyst, *trans*-stilbene was formed in 98%, 97%, 98%, 96%, 97%, 95%, 95%, 96%, 95%, and 94% yield, respectively, clearly illustrating the high stability and excellent reusability of the catalyst. The result is important from a practical point of view.

In summary, we have described the first MCM-41-supported thioether palladium(0) complex whose preparation is rather simple and convenient. This complex has not only high activity and stereoselectivity for arylation reaction of conjugated alkenes with aryl iodides or bromides, but offers practical advantages such as easy handling, separation from the product and reuse. The arylation reaction of styrene, acrylic acid, butyl acrylate and acrylamide with aryl iodides or bromides catalyzed by the MCM-41-S-Pd(0) complex provides a better and practical procedure for the stereoselective synthesis of a variety of *trans*-stilbenes, *trans*-cinnamic acids, *trans*-butyl cinnamates and *trans*-cinnamamides. Work is currently underway to exploit the activity of the MCM-41-S-Pd(0) complex in other palladium-mediated organic syntheses.

3. Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 [9] and 3-(2-cyanoethylsulfanyl)propyltriethoxysilane [10] were conveniently prepared from commercially available and cheap materials according to literature procedures. All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. IR spectra were determined on a Perkin-Elmer 683 instrument. ¹H NMR spectra were recorded on a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard in CDCl₃ or DMSO-d₆ as solvent. X-ray powder diffraction was obtained on Damx-rA (Rigaku). X-ray photoelectron spectra was recorded on XSAM 800 (Kratos).

3.1. 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 CHCl₃ (3 × 20 ml), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me₃SiCl (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.

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

To a solution of PdCl₂ (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 Et₂O (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.

3.3. General procedure for arylation of styrene with aryl halides

A mixture of styrene (0.57 g, 5.5 mmol), aryl halide (5 mmol), Bu₃N (1.11 g, 6 mmol), NMP (2 ml) and the MCM-41-S-Pd(0) complex (43 mg, 0.015 mmol of Pd) was stirred in an oil bath at 100–130 °C for 6–24 h. The mixture was cooled and dissolved in Et₂O (60 ml). The MCM-41-S-Pd(0) complex was separated from the mixture by filtration, washed with distilled water (2 × 10 ml), EtOH (3 × 10 ml) and Et₂O (2 × 10 ml) and reused in the next run. The ethereal solution was washed with 5N HCl (2 × 10 ml), brine (4 × 10 ml) and dried (MgSO₄) and filtered. The solid product formed after concentration of the ethereal solution was recrystallized from EtOH. Spectroscopic data and melting points for the products were compared with those in the literature, showing formation of the appropriate stilbenes.

3.4. General procedure for arylation of acrylic acid with aryl halides

A mixture of acrylic acid (0.40 g, 5.5 mmol), aryl halide (5 mmol), Bu₃N (2.04 g, 11 mmol), NMP (2 ml) and the MCM-41-S-Pd(0) complex (43 mg, 0.015 mmol of Pd) was stirred in an oil bath at 100–130 °C for 6–24 h. After the reaction mixture was cooled, H₂O (20 ml) and NaHCO₃ (1.10 g) were added. After stirring for 10 min, the MCM-41-S-Pd(0) complex was separated from the mixture by filtration. The aqueous phase was separated and acidified with 5N HCl (1.8 ml). After cooling to 0 °C, the solid precipitate was filtered, washed with H₂O (5 × 20 ml) and air dried. Spectroscopic data and melting points for the products were compared with those in the literature confirming formation of the cinnamic acids.

3.5. General procedure for arylation of butyl acrylate with aryl halides

A mixture of butyl acrylate (0.71 g, 5.5 mmol), aryl halide (5 mmol), Bu₃N (1.11 g, 6 mmol), NMP (2 ml) and the MCM-41-S-Pd(0) complex (43 mg, 0.015 mmol of Pd) was stirred in an oil bath at 100–130 °C for 6–24 h. The mixture was cooled and dissolved in Et₂O (60 ml). The MCM-41-S-Pd(0) complex was separated from the mixture by filtration. The ethereal solution was washed with 5N HCl (2 × 10 ml), brine (4 × 20 ml) and dried (MgSO₄) and filtered. The residue formed after concentration

of the ethereal solution was purified by flash column chromatography on silica gel (light petroleum-ethyl acetate 19:1). Spectroscopic data for the products were compared with those in the literature confirming formation of the butyl cinnamates.

3.6. General procedure for arylation of acrylamide with aryl halides

A mixture of acrylamide (0.39 g, 5.5 mmol), aryl halide (5 mmol), Bu₃N (1.11 g, 6 mmol), NMP (2 ml) and the MCM-41-S-Pd(0) complex (43 mg, 0.015 mmol of Pd) was stirred in an oil bath at 100–130 °C for 6–24 h. The reaction mixture was cooled and dissolved in NMP (3.0 ml) and water (1.0 ml). The MCM-41-S-Pd(0) complex was separated from the mixture by filtration. The filtrate was poured into water (100 ml), the precipitated product was isolated by suction and washed with water (3 × 10 ml). The crude product was recrystallized from EtOH. Spectroscopic data and melting points for the products were compared with those in the literature, showing formation of the appropriate cinnamamides.

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