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Short Communication

A phosphine-free heterogeneous formylation of aryl halides catalyzed by a thioether-functionalized MCM-41-immobilized palladium complex

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ABSTRACT

Thioether-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-S-$PdCl_2$] was found to be a highly efficient catalyst for the formylation of aryl iodides or bromides with CO (1 atm) using HCO_2Na as a hydrogen source. This phosphine-free heterogeneous palladium complex can be easily recovered by simple filtration and reused for at least 10 consecutive trials without any decreases in activity.

1. Introduction

Aromatic aldehydes are important building blocks for the synthesis of biologically active molecules or their intermediates [1] and are usually prepared by the electrophilic formylation reactions, however, these methods often suffer from several drawbacks such as the use of unacceptable amount of reagents and producing large quantities of side products and wastes [2,3]. The palladium-catalyzed formylation of aryl halides with carbon monoxide would offer significant advantages over those conventional methods. Schoenberg and Heck reported the first example of $PdX_2(PPh_3)_2$-catalyzed formylation of aryl halides using H_2 as a hydrogen source under high pressures of CO (80–100 bar) at high temperatures (125–150 °C) [4]. The palladium-catalyzed formylation of aryl halides could also be achieved under a lower pressure of carbon monoxide, however, the use of expensive reagents such as silyl [5,6] and tin [7,8] hydrides was required and the formylation with these hydrides is often accompanied by overreduction of the aldehyde and other functional groups due to their high reducing abilities. Singh et al. described reductive carbonylation of aryl and heteroaryl iodides under a syngas atmosphere using $Pd(acac)_2$/dppm as an efficient catalyst [9]. Beller et al. reported an industrially applicable catalytic system containing $Pd(OAc)_2$ and $P(1\text{-adamantyl})_2n\text{Bu}$ (cataCXum®A) for the reductive carbonylation of aryl and heteroaryl bromides using synthesis gas as an environmentally benign formylation source at a comparably low pressure (5 bar) [10–12]. The use of formate salts is probably the best variant to perform palladium-catalyzed formylation of aryl halides since they are very weak reducing agents, cheap and readily available [13,14]. Okano et al. reported that $PdCl_2(PPh_3)_2$-catalyzed formylation of aryl halides with HCO_2Na under CO (1 atm) readily proceeded in DMF to afford the corresponding aldehydes in good yields [15]. However, industrial applications of homogeneous palladium complexes remain a challenge because they are expensive, cannot be recycled, and difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. The immobilization of catalytically active species, i.e. organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst is one potential solution to the latter two problems [16]. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes [17]. Very recently, Tokunaga and coworkers reported a phosphine-free heterogeneous formylation of aryl iodides in the presence of palladium nanoparticles on cobalt oxide under a syngas atmosphere (4 MPa); the catalyst could be reused at least 7 times without significant loss of activity [18].

Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [19,20]. To date, some palladium complexes on functionalized MCM-41 support have been prepared and successfully used in carbon–carbon coupling reactions [21–24]. However, to the best of our knowledge, the formylation of aryl halides with carbon monoxide catalyzed by immobilization of palladium in MCM-41 has not been reported in the previous literature. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a thioether-functionalized MCM-41-immobilized palladium(II) complex,

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which was used as an effective, phosphine-free heterogeneous palladium catalyst for the formylation of aryl halides under an atmospheric pressure of carbon monoxide using HCO_2Na as a hydrogen source.

2. Experimental

All chemicals were obtained from commercial suppliers and used as received, unless otherwise noted. The mesoporous material MCM-41 [25] and ω-(methylmercapto)undecyltrimethoxysilane [26] were prepared according to literature procedures. All solvents were distilled and dried before use.

2.1. Preparation of the catalyst

2.1.1. Preparation of MCM-41-S

A solution of ω-(methylmercapto)undecyltrimethoxysilane (2.0 g, 6.2 mmol) in dry chloroform (18 mL) was added to a suspension of the MCM-41 (2.5 g) in dry toluene (180 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (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 120 °C for 5 h to obtain 3.64 g of hybrid material MCM-41-S. The sulfur content was found to be 1.07 mmol g^{-1} by elemental analysis.

2.1.2. Preparation of MCM-41-S-$PdCl_2$

In a small Schlenk tube, MCM-41-S (2.5 g) was mixed with $PdCl_2$ (0.158 g, 0.89 mmol) in dry acetone (50 mL). The mixture was refluxed for 72 h under Ar. The solid product was filtered by suction, washed with distilled water and acetone and dried at 70 °C/26.7 Pa under Ar for 5 h to give 2.57 g of a yellow palladium complex [MCM-41-S-$PdCl_2$]. The sulfur and palladium contents were found to be 0.91 mmol g^{-1} and 0.29 mmol g^{-1}, respectively.

2.2. Characterization techniques of the catalyst

Microanalyses were measured by using a PerkinElmer 2400 II CHNS elemental analyzer. Palladium content was determined with an inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos). X-ray powder diffraction patterns were obtained on D/Max-rA (Rigaku). The BET surface area and pore analysis were performed on ASAP2010 (micromeritics) by N_2 physical adsorption–desorption at 77.4 K.

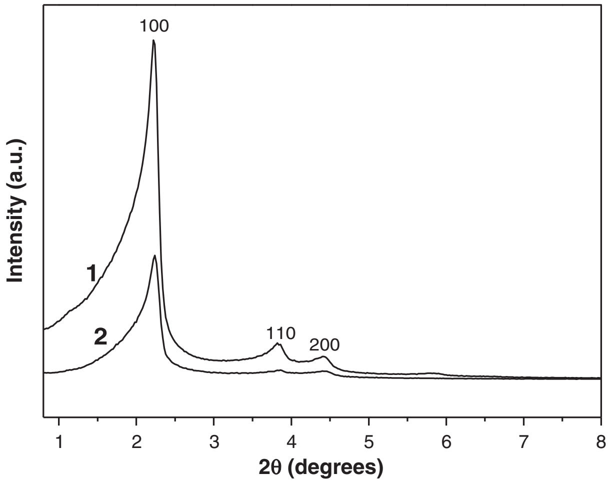


Fig. 1. XRD patterns of the parent MCM-41 (1) and MCM-41-S-$PdCl_2$ (2).

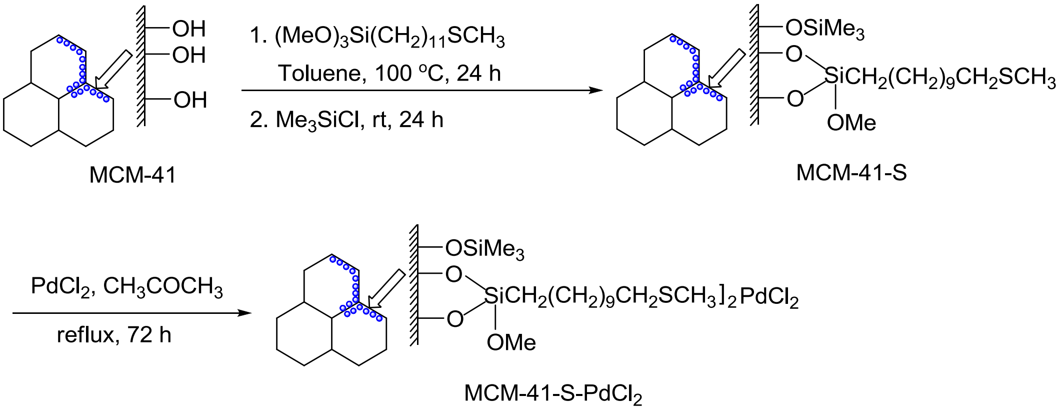
2.3. General procedure for the formylation of aryl iodides or bromides

A 50 mL round-bottomed flask equipped with a gas inlet tube, a reflux condenser, and a magnetic stirring bar was charged with MCM-41-S-$PdCl_2$ (173 mg, 0.05 mmol Pd), aryl halide (5.0 mmol) and HCOONa (7.5 mmol). The flask was flushed with carbon monoxide. DMF (5 mL) was added by syringe and a slow stream of CO was passed into the suspension. The mixture was vigorously stirred at 100–110 °C for 4–24 h, cooled to room temperature, and diluted with diethyl ether (50 mL). The palladium catalyst was separated from the mixture by filtration, washed with distilled water (2 × 10 mL), ethanol (2 × 10 mL) and ether (2 × 10 mL) and reused in the next run. The ethereal solution was washed with water (3 × 20 mL) and dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10:1).

All formylation products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent.

3. Results and discussion

Although phosphine ligands stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course phosphine-free systems. It is known that the catalysts



Scheme 1. Preparation of the MCM-41-S-$PdCl_2$ complex.

Table 1
XPS data for MCM-41-S-PdCl$_2$, MCM-41-S, PdCl$_2$, metal Pd and used catalyst.[a]

Sample	Pd$_{3d5/2}$	S$_{2p}$	Si$_{2p}$	O$_{1s}$	Cl$_{2p}$
MCM-41-S-PdCl$_2$	337.5	164.2	103.2	533.1	199.3
MCM-41-S		163.7	103.2	533.0	
PdCl$_2$	338.3				199.2
Metal Pd	335.2				
Used catalyst	336.5	164.3	103.1	533.2	

[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.

Table 2
Reaction condition screening for the formylation reaction of iodobenzene with HCO$_2$Na.[a]

Entry	Solvent	Pd catalyst (mol%)	Temp. (°C)	Time (h)	Yield[b] (%)	TON	TOF
1	DMF	1.0	25	24	0	0	0
2	DMF	1.0	60	24	Trace	0	0
3	DMF	1.0	80	24	56	56	2.3
4	DMF	1.0	100	8	84	84	10.5
5	DMF	1.0	110	5	81	81	16.2
6	Toluene	1.0	100	24	0	0	0
7	Dioxane	1.0	100	24	Trace	0	0
8	DMSO	1.0	100	12	51	51	4.3
9	Propionitrile	1.0	100	24	Trace	0	0
10	Pyridine	1.0	100	24	7	7	0.3
11	DMF	2.0	100	5	83	41.5	8.3
12	DMF	0.5	100	20	78	156	7.8

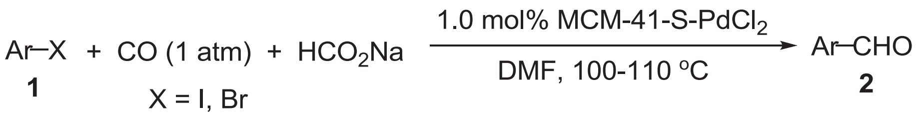
[a] All reactions were performed using PhI (5.0 mmol) and HCO$_2$Na (7.5 mmol) in a solvent (5.0 mL) under CO (1 atm).
[b] Isolated yield.

containing phosphine ligands at higher temperatures are unstable [27] and the procedure for preparing the supported phosphine palladium complexes is rather complicated. Therefore, the development of novel phosphine-free heterogeneous palladium catalysts having a high activity and good stability is a topic of enormous importance. A new thioether-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-S-PdCl$_2$] was prepared from ω-(methylmercapto)-undecyltrimethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride (Scheme 1). The X-ray powder diffraction (XRD) analysis of the MCM-41-S-PdCl$_2$ indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41 (Fig. 1). The nitrogen adsorption studies demonstrated that significant decreases in surface area and pore size by virtue of modification of the MCM-41 were observed. The MCM-41 had a surface area of 906.4 m^2 g^{-1} and a diameter of 2.8 nm, however, MCM-41-S-PdCl$_2$ had a surface area of 642.7 m^2 g^{-1} and a diameter of 2.1 nm.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the new thioether-functionalized MCM-41-immobilized palladium(II) complex. The S:Pd mole ratio of the MCM-41-S-PdCl$_2$ was determined to be 3.14. The XPS data for MCM-41-S-PdCl$_2$, MCM-41-S, PdCl$_2$ and metal Pd are listed in Table 1. It can be seen that the difference of S$_{2p}$ binding energies between MCM-41-S-PdCl$_2$ and MCM-41-S is 0.5 eV, and the binding energy of Pd$_{3d5/2}$ in MCM-41-S-PdCl$_2$ is 0.8 eV less than that in PdCl$_2$, but 2.3 eV larger than that in metal Pd. These results show that a coordination bond between S and Pd is formed in the MCM-41-S-PdCl$_2$. To verify whether the resting state of the catalyst is Pd(0) or Pd(II), the XPS of used catalyst was also measured and listed in Table 1. The shift (lower) of the Pd$_{3d5/2}$ binding energy of used catalyst indicated that the resting state of the catalyst should be Pd(0).

The formylation of iodobenzene with HCO$_2$Na was chosen as a model reaction, and the influences of solvents, reaction temperatures, and catalyst quantities on the reaction were tested. The results are summarized in Table 2. For the temperatures tested [25, 60, 80, 100, and 110 °C], 100 °C gave the best result. Among the solvents evaluated [toluene, dioxane, pyridine, propionitrile, DMF, and DMSO], DMF was found to be the most effective. Less polar solvents such as toluene, dioxane, pyridine and propionitrile were not favorable for the formylation, and DMSO afforded a moderate yield (entry 8). The amount of palladium catalyst was also screened, and 1.0 mol% loading of palladium was found to be optimal (entry 4), a lower yield was observed when the amount of the catalyst was decreased (entry 12). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of benzaldehyde (entry 11). Thus, the optimized reaction condition for this formylation reaction is the MCM-41-S-PdCl$_2$ (1.0 mol%) with DMF as solvent at 100 °C under CO (1 atm) for 8 h (entry 4).

To examine the scope for this heterogeneous formylation, we have investigated the reaction of a variety of aryl iodides or bromides with HCO$_2$Na under the optimized reaction conditions (Scheme 2) and the results are outlined in Table 3. As shown in Table 3, the formylation reactions of a variety of aryl iodides with HCO$_2$Na under CO (1 atm) proceeded smoothly in DMF at 100 °C affording the corresponding aromatic aldehydes **2a–l** in good to excellent yields (entries 1–12). Various electron-donating and electron-withdrawing groups such as $-OCH_3$, $-CH_3$, $-Cl$, $-CN$, $-CO_2CH_3$, $-NO_2$, $-CF_3$, and $-COCH_3$ on aryl iodides were well tolerated. The reactivity of electron-deficient aryl iodides was higher than that of electron-rich aryl iodides. The reactions of sterically hindered aryl iodides such as 2-iodoanisole, methyl 2-iodobenzoate and 2-trifluoromethyliodobenzene could also give the corresponding aromatic aldehydes **2m–o** in good yields on longer times (entries 13–15). The formylation of the bulky 1-iodonaphthalene afforded 1-naphthaldehyde **2p** in 86% yield (entry 16). The heteroaryl iodides such as 3-iodopyridine and 2-iodothiophene could undergo the formylation to give pyridine-3-carboxaldehyde **2q** and thiophene-2-carboxaldehyde **2r** in 79% and 85% yields, respectively (entries 17 and 18). Aryl bromides were less reactive than the iodides, and underwent the formylation at 110 °C to give the corresponding aromatic aldehydes in good yields along with about 4–9% yields of reductive dehalogenation by-products (entries 19–25). Benzyl bromide could also undergo the formylation at 100 °C to afford phenylacetaldehyde **2s** in an 84% yield (entry 26). To compare the reactivity of the MCM-41-S-PdCl$_2$ with that of some commercially available heterogeneous palladium catalysts such as Pd/C (from Aldrich), we also performed the formylation of iodobenzene using Pd/C as the catalyst under the same conditions. It was found that the formylation reaction did not occur with Pd/C instead of MCM-41-S-PdCl$_2$. In contrast to the iodides and bromides, the chlorides were inactive under these conditions. Therefore, both 4-chloroiodobenzene and 4-bromochlorobenzene were formylated selectively to 4-chlorobenzaldehyde **2b** in high yields (entries 2 and 20).



$$\underset{\mathbf{1}}{\text{Ar–X}} + \text{CO (1 atm)} + \underset{\text{X = I, Br}}{\text{HCO}_2\text{Na}} \xrightarrow[\text{DMF, 100-110 °C}]{\text{1.0 mol\% MCM-41-S-PdCl}_2} \underset{\mathbf{2}}{\text{Ar–CHO}}$$

Scheme 2. Heterogeneous formylation of aryl halides with HCO$_2$Na.

Table 3
Formylation of aryl halides with HCO_2Na under CO (1 atm) catalyzed by MCM-41-S-$PdCl_2$.[a]

Entry	Ar	X	Temp. (°C)	Time (h)	Product	Yield[b] (%)	TON	TOF
1	Ph	I	100	8	**2a**	84	84	10.5
2	4-ClC_6H_4	I	100	6	**2b**	88	88	14.7
3	4-MeC_6H_4	I	100	10	**2c**	83	83	8.3
4	4-$MeOC_6H_4$	I	100	12	**2d**	81	81	6.8
5	4-CNC_6H_4	I	100	6	**2e**	90	90	15.0
6	3-MeC_6H_4	I	100	10	**2f**	84	84	8.4
7	3-$MeOC_6H_4$	I	100	12	**2g**	82	82	6.8
8	4-$MeCOC_6H_4$	I	100	6	**2h**	91	91	15.2
9	4-$MeOCOC_6H_4$	I	100	6	**2i**	89	89	14.8
10	4-$NO_2C_6H_4$	I	100	4	**2j**	93	93	23.3
11	3-$NO_2C_6H_4$	I	100	6	**2k**	87	87	14.5
12	3-$CF_3C_6H_4$	I	100	7	**2l**	85	85	12.1
13	2-$MeOC_6H_4$	I	100	24	**2m**	75	75	3.1
14	2-$MeOCOC_6H_4$	I	100	20	**2n**	80	80	4.0
15	2-$CF_3C_6H_4$	I	100	24	**2o**	72	72	3.0
16	1-Naphthyl	I	100	12	**2p**	86	86	7.2
17	3-Pyridinyl	I	100	10	**2q**	79	79	7.9
18	2-Thienyl	I	100	12	**2r**	85	85	7.1
19	Ph	Br	110	12	**2a**	75	75	6.3
20	4-ClC_6H_4	Br	110	10	**2b**	79	79	7.9
21	4-CNC_6H_4	Br	110	10	**2e**	82	82	8.2
22	4-$MeCOC_6H_4$	Br	110	10	**2h**	83	83	8.3
23	4-$MeOCOC_6H_4$	Br	110	10	**2i**	81	81	8.1
24	4-MeC_6H_4	Br	110	16	**2c**	74	74	4.6
25	4-$MeOC_6H_4$	Br	110	24	**2d**	71	71	2.9
26	$PhCH_2$	Br	100	6	**2s**	84	84	14.0

[a] All reactions were performed using aryl halide (5.0 mmol), HCO_2Na (7.5 mmol), and MCM-41-S-$PdCl_2$ (0.05 mmol) in DMF (5.0 mL) under CO (1 atm).
[b] Isolated yield.

To verify whether the observed catalysis was due to the heterogeneous catalyst or to a leached palladium species in a solution, we performed the hot filtration test [28]. We focused on the formylation of iodobenzene with HCO_2Na. We filtered off the MCM-41-S-$PdCl_2$ complex after 4 h of reaction time and allowed the filtrate to react further. We found that, after this hot filtration, no further reaction was observed, indicating that leached palladium species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no palladium could be detected in the hot filtered solution.

The MCM-41-S-$PdCl_2$ complex can be easily recovered by a simple filtration of a reaction solution. We also investigated the possibility to reuse the catalyst by using the formylation of 4-iodoacetophenone. It was found that when the reaction of 4-iodoacetophenone with HCO_2Na under CO (1 atm) was performed even with 1.0 mol% of MCM-41-S-$PdCl_2$, the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave **2h** in an 89% yield (Table 4, entry 2). The average yield of **2h** in consecutive reactions promoted by the 1st through the 10th recycled catalysts was 90% (Table 4, entry 3).

4. Conclusions

In summary, we have developed a novel, practical and environmentally friendly catalytic system for formylation of aryl halides under CO (1 atm) by using thioether-functionalized MCM-41-immobilized palladium complex as the catalyst with HCO_2Na as a hydrogen source. The reactions generated a variety of aromatic aldehydes in good to excellent yields. This novel phosphine-free heterogeneous palladium catalyst can be easily prepared and exhibits high catalytic activity and can be reused at least 10 times without any decreases in activity.

Acknowledgments

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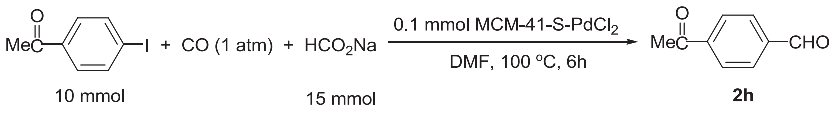
Table 4
Formylation of 4-iodoacetophenone with HCO_2Na under CO (1 atm) catalyzed by a recycled catalyst.



Entry	Catalyst cycle	Isolated yield (%)	TON	TOF
1	1st	91	91	15.2
2	10th	89	89	14.8
3	1st to 10th consecutive	Av 90	Total of 900	

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