

A Highly Active Heterogeneous Palladium Catalyst for the Suzuki–Miyaura and Ullmann Coupling Reactions of Aryl Chlorides in Aqueous Media**

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Palladium-catalyzed carbon-carbon (C–C) coupling reactions of aryl halides, such as Suzuki–Miyaura and Ullmann reactions, are very important as versatile routes to constructing biaryl units in organic synthesis.^[1] Although homogeneous palladium catalysts have been extensively investigated, industrial applications of these reactions remain challenging because the catalysts are expensive, cannot be recycled, and are difficult to separate from the product mixture,^[1,2] which is a particular drawback for applications in the pharmaceutical industry; heterogeneous palladium catalysts are a promising solution to these problems. A number of solid materials,^[3] such as carbon structures,^[4] polymers,^[5] and mesoporous silica^[6] have been employed as supports for palladium. Numerous heterogeneous palladium catalysts have been utilized in the coupling reactions of aryl bromides or iodides;^[1b] nevertheless, only a very limited number of such palladium catalysts have been reported for coupling reactions with aryl chlorides.^[7] From a practical point of view, the use of aryl chlorides is desirable because they are inexpensive and readily available.^[1] However, the activation of aryl chlorides is much more difficult than aryl bromides or iodides. Furthermore, the reported coupling reactions were mostly carried out in organic solvents. From a sustainable chemistry viewpoint, the use of water instead of volatile organic solvents is particularly important. Therefore, the development of heterogeneous catalysts that can activate aryl chlorides and facilitate the coupling reactions of aryl chlorides in aqueous media is highly desirable.^[1]

Metal-organic frameworks (MOFs) have emerged as a particular class of functional materials owing to their high surface area, porosity, and chemical tunability.^[8] Because of these properties, MOFs have promising applications in heterogeneous catalysis. However, over the past decade, most of the research efforts have been focused on preparing new MOFs and studying their applications in gas storage and separation.^[9] So far, there are a relatively limited number of

reports on MOFs as catalysts and even fewer reports on supporting noble metal nanoparticles (NPs) on MOFs as catalysts for heterogeneous catalysis.^[10] A palladium-containing MOF (Pd-MOF) has been reported to be an active catalyst for the Suzuki–Miyaura coupling reaction of aryl bromides.^[11] To the best of our knowledge, there are currently no reports of employing MOFs as supports for metal NPs in Suzuki–Miyaura and Ullmann coupling reactions of aryl chlorides.

Herein, we report the water-mediated coupling reactions of aryl chlorides over a heterogeneous palladium catalyst, which is deposited on a zeolite-type MOF. This work represents the first example of an active catalyst, comprised of a MOF as a support for metal NPs, for the coupling reactions of aryl chlorides. We have chosen MIL-101 ($\text{Cr}_3\text{-(F,OH)(H}_2\text{O)}_2\text{O}[(\text{O}_2\text{C})\text{-C}_6\text{H}_4\text{-(CO}_2\text{)}]_3\text{,}n\text{H}_2\text{O}$ ($n \approx 25$)) because it has a large surface area (BET, ca. $4000\text{ m}^2\text{ g}^{-1}$),^[12] which is desirable for depositing small palladium NPs. Furthermore, the hybrid pore surface, which constitutes both hydrophilic and hydrophobic networks,^[13] and the large pore size (ca. 30 Å) may facilitate the selective adsorption of an aryl substrate in water and mass transfer inside the pores. Moreover, MIL-101 is stable when exposed to indoor ambient air and treated with various organic solvents.^[12,14]

MIL-101 was synthesized and purified according to the reported procedure.^[12] Supported palladium NPs were prepared by impregnation of activated MIL-101 with a $\text{Pd}(\text{NO}_3)_2$ precursor that was diluted in *N,N*-dimethylformamide (for experimental details, see the Supporting Information). The palladium loading (ca. 1 wt %) did not result in any apparent loss of crystallinity in the X-ray diffraction patterns (see the Supporting Information), indicating that the integrity of the MIL-101 framework was maintained. The TEM image, shown in Figure 1, shows that the palladium NPs were highly

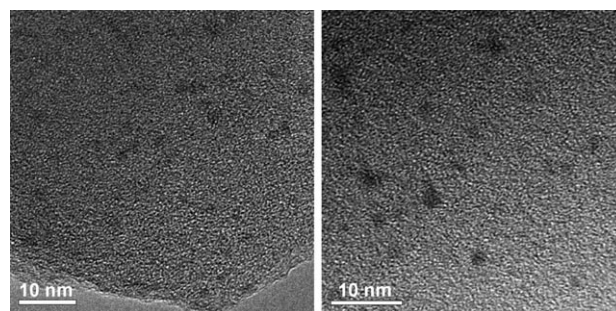


Figure 1. TEM images of Pd/MIL-101 before the reaction (left) and after five cycles (right).

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dispersed, with a mean diameter of (1.9 ± 0.7) nm, as estimated by size distribution (see the Supporting Information). The slight decreases in the amount of N_2 adsorption and pore size indicate that the cavities of MIL-101 could be occupied by highly dispersed palladium NPs and/or blocked by palladium NPs that were located at the surface (see the Supporting Information), as in the case of metal NPs loaded onto MOF-5, ZIF-8, and zeolitic materials.^[10d,15] The XPS investigation of Pd/MIL-101 at the palladium 3d level indicated that most of the palladium was in the reduced form (see the Supporting Information).

It is well known that activation of C–Cl bond is much more difficult than C–Br and C–I bonds, and in general requires harsher reaction conditions in heterogeneous catalysis system.^[1] Herein, 4-chloroanisole, a deactivated aryl chloride, was employed as the substrate in the screening of Suzuki–Miyaura coupling reaction parameters over Pd/MIL-101. The reaction was first tested on the Suzuki–Miyaura coupling reaction of 4-chloroanisole with phenylboronic acid using K_2CO_3 as base in neat water at 80 °C. Only trace amounts of cross-coupling product were formed in 6 hours (Table 1, entry 1). The addition of tetrabutylammonium

Table 1: Suzuki–Miyaura coupling of 4-chloroanisole with Pd/MIL-101.^[a]

$\text{MeO}-\text{C}_6\text{H}_4-\text{Cl} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{H}_2\text{O}]{\text{Pd/MIL-101}} \text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{OMe}$				
Entry	Base	TBAB [mmol] ^[b]	t [h]	Yield [%] ^[c]
1	K_2CO_3	0	6	< 3
2	K_2CO_3	0.1	6	43
3	K_3PO_4	0.1	6	< 3
4	KF	0.1	6	23
5	CS_2CO_3	0.1	6	21
6	Na_2CO_3	0.1	6	< 3
7	NaOH	0.1	6	11
8	Et_3N	0.1	6	17
9	NaOMe	0.1	6	65
10	NaOMe	0.3	6	82
11	NaOMe	0	6	43
12	NaOMe	0	20	78
13 ^[d]	NaOH	0.1	6	63

[a] Reaction conditions: 4-chloroanisole (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), water (4 mL), and Pd/MIL-101 (0.9 mol % Pd), 80 °C, under N_2 . [b] Tetrabutylammonium bromide. [c] Determined by GC analysis against an internal standard. [d] Methanol (1.5 mmol) was added.

bromide (TBAB) enhanced the yield significantly (Table 1, entry 2), presumably owing to the stabilization effect of the palladium NPs.^[7a,b,16] To determine the optimal experimental conditions, the impact of various bases on the efficiency of this process was studied because the nature of the base is known to be crucial in this type of coupling reaction (Table 1, entries 3–9). The highest yield was obtained when the reaction was carried out using NaOMe as a base (Table 1, entry 9). With NaOMe, a further increase in the amount of TBAB significantly enhanced the conversion of 4-chloroanisole, giving a good yield (82 %) of the cross-coupling product in 6 hours (Table 1, entry 10). It is noteworthy that the catalyst could activate 4-chloroanisole effectively, even in the absence

of TBAB when NaOMe was used as base (Table 1, entries 11 and 12). Complete conversion into the desired product is expected with a prolonged reaction time. The much higher yield achieved with NaOMe (Table 1, entry 9) as compared with NaOH (Table 1, entry 7) may be due to the presence of a small amount of methanol that is formed from the reaction of NaOMe with water; the combination of NaOH with methanol was also efficient in the Suzuki–Miyaura coupling reaction (Table 1, entry 13).

To investigate the scope of aryl chlorides that could be tolerated in the Suzuki–Miyaura coupling reaction with phenylboronic acid, different aryl chlorides were employed in the reaction (Table 2). High catalytic activities were

Table 2: Suzuki–Miyaura coupling reactions of aryl chlorides over supported palladium catalysts.^[a]

$R-\text{C}_6\text{H}_4-\text{Cl} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{H}_2\text{O}]{[\text{Pd}] \text{ Catalyst}} R-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$			
Entry	Aryl chloride	Product	Yield [%] ^[b]
1	$\text{C}_6\text{H}_5-\text{Cl}$	$\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$	97 (99)
2	$\text{MeO}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{MeO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	96 (99)
3	$\text{MeOC}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{MeOC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	96 (99)
4	$\text{C}_6\text{H}_4(\text{OMe})-\text{Cl}$	$\text{C}_6\text{H}_4(\text{OMe})-\text{C}_6\text{H}_5$	81 (83)
5	$\text{MeO}-\text{C}_6\text{H}_4-\text{Br}$	$\text{MeO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	95 (98)
6 ^[c]	$\text{MeO}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{MeO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	< 3
7 ^[d]	$\text{MeO}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{MeO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	35 (39)
8 ^[e]	$\text{MeO}-\text{C}_6\text{H}_4-\text{Cl}$	$\text{MeO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	16 (21)

[a] Reaction conditions: aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol), NaOMe (1.5 mmol), TBAB (0.3 mmol), water (4 mL), and Pd/MIL-101 (0.9 mol % Pd), 80 °C, 20 hours, under N_2 . [b] Yield of isolated product (GC yield in parenthesis). [c] Pd^{II}/MIL-101 (0.9 mol % Pd). [d] Pd/C (0.9 mol % Pd). [e] Pd/ZIF-8 (0.9 mol % Pd).

observed for chlorobenzene and both electron-rich and electron-poor aryl chlorides, affording the corresponding biphenyl compounds in excellent yields in 20 hours under the optimized reaction conditions (Table 2, entries 1–3). It should be noted that 2-chloroanisole, which is both deactivated and sterically hindered, could also be coupled in good yield in 20 hours (Table 2, entry 4). More-reactive aryl bromides were also smoothly coupled to give their corresponding products (Table 2, entry 5). However, the unreduced Pd^{II}/MIL-101 afforded essentially no C–C bond formation (Table 2, entry 6), indicating that palladium in the reduced form is the active site for the Suzuki–Miyaura coupling reaction. XPS analysis of the Pd^{II}/MIL-101 catalyst after the reaction revealed that the reduction of Pd^{II} to Pd⁰ was not significant under the reaction conditions (see the Supporting Information).

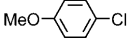
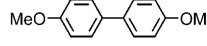
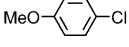
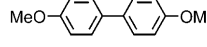
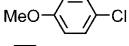
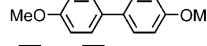

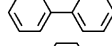
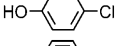
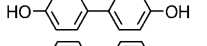
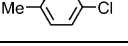
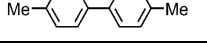
For comparison, a commercial Pd/C catalyst (1 wt % palladium) was tested under the same reaction conditions

(Table 2, entry 7); only 35 % yield of cross-coupled product was obtained using Pd/C in the coupling of 4-chloroanisole with phenylboronic acid. In some reports, Pd/C has been found to work efficiently for the coupling reaction of 4-chloroanisole in aqueous media at 140 °C.^[7a,b] The much-lower activity obtained in this study is probably due to the lower reaction temperature than that used previously. Furthermore, the different palladium source could be another cause for the diverse activities.^[7b] Low activity was also observed for palladium-supported ZIF-8 (Zn(MeIM)₂, MeIM = 2-methylimidazole),^[9a] one of representative MOFs with a surface area of 1398 m² g⁻¹ and pore size of 11 Å (Table 2, entry 8). The much higher activity of Pd/MIL-101, as compared to Pd/ZIF-8, may be attributed to the larger surface area and pore size of MIL-101, which ensured the high dispersion of palladium active sites and facilitated the diffusion of reactants and large product molecules in the pores. Moreover, the enhanced surface Lewis acidity on MIL-101 owing to the open metal (Cr³⁺) sites^[10b,g] would favor the adsorption of the chloroaryl molecules, and thus enhance the activity. As previously reported, the Al³⁺ ions that were incorporated into MCM-41 may serve as Lewis-type acidic sites that may adsorb iodoaryl molecules easily by the donation of the *para* electrons in the benzene ring.^[17]

The atmosphere in which the reaction was performed had a significant impact on the efficiency of the Suzuki–Miyaura coupling process. Performing the coupling of 4-chloroanisole with phenylboronic acid reaction in open air resulted in a much lower yield of cross-coupling product (ca. 33 %) than when the reaction was performed under a nitrogen atmosphere (ca. 96 %, see Table 2, entry 2). This may be due to the oxidation and homocoupling of phenylboronic acid by molecular oxygen^[18] that was dissolved in water over Pd/MIL-101, because some phenol and biphenyl side-products were formed in the reaction. Most interestingly, we detected large amounts (ca. 66 % selectivity) of 4,4'-dimethoxy biphenyl, which might be formed from the homocoupling of 4-chloroanisole. These results indicate that a low ratio of phenylboronic acid to 4-chloroanisole in the reactant mixture favored the homocoupling process in a competition between the homo- and cross-coupling reactions of 4-chloroanisole. This was confirmed by comparing the results obtained with different ratios of phenylboronic acid to 4-chloroanisole (see the Supporting Information).

Encouraged by these interesting results, we examined the catalytic activity of Pd/MIL-101 for the Ullmann homocoupling reaction of 4-chloroanisole in the absence of phenylboronic acid under similar reaction conditions to those used for the Suzuki coupling reactions. 4-Chloroanisole was coupled to 4,4'-dimethoxy biphenyl in quantitative yield under a nitrogen atmosphere (Table 3, entry 1). In the reaction system, the reducing agent for the regeneration of Pd⁰ could be the methanol produced from the reaction of NaOMe with water. As demonstrated by a number of reports, alcohols (such as ethanol or isopropanol) can be used as reducing agents for Ullmann homocoupling.^[19] It should be noted that an excellent yield of 96 % was achieved even when the reaction was carried out in air (Table 3, entry 2); however, the unreduced Pd^{II}/MIL-101 catalyst was ineffective under these

Table 3: Ullmann coupling reactions of aryl chlorides over supported palladium catalysts.^[a]

$\text{R}-\text{C}_6\text{H}_4-\text{Cl} \xrightarrow[\text{H}_2\text{O}]{\text{Pd Catalyst}} \text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{R}$			
Entry	Aryl chloride	Product	Yield [%] ^[b]
1 ^[c]			97 (99)
2			96 (98)
3 ^[d]			< 3
4			96 (98)
5			96 (99)
6			95 (97)

[a] Reaction conditions: Aryl chloride (1.0 mmol), NaOMe (1.5 mmol), TBAB (0.3 mmol), water (4 mL), Pd/MIL-101 (0.5 mol % Pd), 80 °C, 20 hours, under air. [b] Yield of isolated product (GC yield in parenthesis). [c] The reaction was carried out under a N₂ atmosphere. [d] Pd^{II}/MIL-101 (0.5 mol % Pd) was used.

conditions (Table 3, entry 3). These results indicate that palladium in its reduced form is the active site for the Ullmann coupling reaction, and the oxidation of metallic palladium was not significant during the reaction in air.

Various aryl chlorides, such as chlorobenzene, 4-chlorophenol, and 4-chlorotoluene were also examined as substrates for the Ullmann coupling reaction in air (Table 3, entries 4–6). The conversion was essentially quantitative, with 100 % selectivity to the corresponding biphenyl compound at 80 °C for all three substrates. It should be mentioned that the symmetrical biaryl compounds are important intermediates for synthesizing agrochemicals, pharmaceuticals, and natural products. Wan et al. recently reported a highly active heterogeneous palladium/silica-carbon catalyst for the Ullmann coupling of chlorobenzene that afforded 100 % conversion into the biphenyl product with moderate selectivity (64 %) in water and air at 100 °C.^[20] Our Pd/MIL-101 catalyst gave exceptionally high activity and selectivity for the Ullmann coupling of aryl chlorides using water as the solvent at a moderate temperature (80 °C), thus showing great potential for practical applications.

The Pd/MIL-101 catalyst can be easily recovered and reused in the Ullmann coupling of 4-chloroanisole five times without any loss of efficiency (see the Supporting Information). The crystalline structure of the catalyst was mostly retained after five catalytic cycles (see the Supporting Information). A TEM image of the reused catalyst (Figure 1) indicates that the mean diameter of the nanoparticles is (2.0 ± 0.6) nm (see the Supporting Information), which is very similar to that before reaction. This result indicates that no sintering of palladium NPs occurred during the reaction. The liquid phase of the reaction mixture was collected by hot filtration after the reaction and analyzed by atomic absorption spectroscopy (AAS). A very low amount of dissolved palladium (less than 0.2 % of the total palladium) was detected in the solution at the end of the reaction. Moreover, the catalyst was removed from the solution after

approximately 50% conversion at the reaction temperature. The isolated solution did not exhibit any further reactivity under similar reaction conditions. These studies indicate that the loss of palladium active sites is negligible, which could account for the preservation of catalytic activity.

In conclusion, we have developed a highly efficient heterogeneous catalyst system for the water-mediated Suzuki–Miyaura and Ullmann coupling reactions of aryl chlorides using porous MOF-supported palladium NPs as the catalyst. Furthermore, the catalyst is stable, shows negligible metal leaching, and maintains high catalytic activities over a number of cycles. The use of MOFs as catalyst supports might bring new opportunities in the development of highly active heterogeneous palladium catalysts for C–C coupling or other palladium-catalyzed reactions. Studies aimed at extending the scope of Pd/MIL-101 to other organic transformations are currently underway in our laboratories.

Experimental Section

MIL-101 was prepared from the hydrothermal reaction of Cr-(NO₃)₃·9H₂O, terephthalic acid, HF, and water at 220 °C for 8 hours. The powder was purified by post-reaction hydrothermal treatment using hot ethanol (see the Supporting Information). Supported palladium was prepared by impregnation of activated MIL-101 with the desired amount of Pd(NO₃)₂ diluted in *N,N*-dimethylformamide at room temperature. The impregnated MIL-101 sample was washed with *N,N*-dimethylformamide and slowly dried in air. The as-synthesized sample was further dried at 150 °C for 8 hours, followed by placing under a stream of H₂ at 200 °C for 2 hours to yield Pd/MIL-101. The palladium loading on the sample was 0.99 wt %, based on atomic absorption spectroscopy (AAS) analysis. Detailed methods for preparation and characterization are described in the Supporting Information.

Typical procedure for Suzuki–Miyaura coupling reaction: Aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), NaOMe (1.5 mmol), TBAB (0.3 mmol), and palladium catalyst (0.9 mol %) were added to 4 mL deionized water. The reaction mixture was stirred at the desired temperature under a N₂ atmosphere. The solution was filtered and washed with brine and diethyl ether. The organic phase was subsequently extracted with diethyl ether (3 × 20 mL), dried over MgSO₄, and concentrated in vacuo. The crude product was quantified by GC-MS analysis. The product was purified by chromatography on silica gel and characterized by GC-MS and ¹H NMR spectroscopy.

Typical procedure for the Ullmann coupling reaction: Aryl halide (1.0 mmol), NaOMe (1.5 mmol), and TBAB (0.3 mmol) were mixed in deionized water (4 mL) before the palladium catalyst (0.5 mol %) was added to the reaction vessel. The reaction mixture was stirred at 80 °C under air. To test the recyclability of the catalyst, the Ullmann coupling reactions were performed with 4-chloroanisole, using the same reaction conditions as described above, except using the recovered catalyst each time. The catalyst was isolated from the reaction solution at the end of each cycle, washed with water and toluene, and then dried under vacuum at 150 °C. The dried catalyst was then reused in a subsequent run. Detailed methods for catalytic measurements and analysis are described in the Supporting Information.

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