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Facile synthesis of palladium nanoparticles encapsulated in amine-functionalized mesoporous metal–organic frameworks and catalytic for dehalogenation of aryl chlorides

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A B S T R A C T

Highly dispersed palladium nanoparticles (Pd NPs) encapsulated in the mesoporous cages of amine -functionalized metal–organic frameworks (MOFs) MIL-101(Cr)–NH_2 have been prepared using an anion-exchange method. The Pd NPs were characterized by powder X-ray diffraction, N_2 adsorption, CO chemisorption, transmission electron microscopy, inductively coupled plasma atomic emission spectroscopy, and X-ray photoelectron spectroscopy. The particles size (2.49 nm) of the obtained Pd NPs was in good agreement with the cage diameters (2.9 nm and 3.4 nm). The resulting Pd/MIL-101(Cr)–NH_2 catalysts exhibited extremely high catalytic activities in the dehalogenation of aryl chlorides in water under mild conditions. Moreover, the Pd NPs confined in mesoporous cages is easily recoverable and can be reused several times without leaching and loss of activity.

1. Introduction

Aryl halides are commonly used as solvents, insect repellents, fungicides, and organic intermediates [1]. However, these aryl halides (especially some priority pollutants) are high risk to our health and environment due to their toxicity and strong bioaccumulation potential [1–4]. Unfortunately, incineration is unattractive from the environmental standpoint that some products such as dioxins are even more toxic than the aryl halides, which are also not readily biodegradable [1,5]. Therefore, great efforts have been devoted to developing methods for dehalogenating aryl halides, which leads to a drastic decrease in toxicity [6–8]. Generally, there are several methods for solving the problem [9]: the available techniques mainly include wet catalytic oxidation [10,11], photochemical treatment [12], and palladium [1,4–9,13–28] catalytic hydrogenation. Recently, an operationally simple iron-catalyzed hydrodehalogenation of aryl halides has also been developed [29–32]. Among the various detoxification techniques available up to now, palladium-catalyzed hydrodechlorination is an interesting one that can be employed to treat streams containing concentrated or dilute chlorinated organic pollutants under lower temperature and pressure and resistance to deactivation [16,17].

Palladium catalytic homogeneous systems for hydrodechlorination of aryl chlorides have already been used in industrial decontamination under H_2 pressure or strong bases such as hydroxides [33]. However, the expensive palladium catalyst in such a homogeneous form cannot be recovered and is difficult to separate from the products. In contrast, heterogeneous palladium catalysts have been proven to be promising alternatives for avoiding these problems [9]. Various materials, such as Al_2O_3 [21], carbon structures [9,14,20,22,25,26], polymers [16,17], mesoporous silica [1,24], zeolites [19], magnetic materials [15], and ionic liquids [18], have been employed as supports for palladium catalysts. Compared with other heterogeneous catalysts, palladium nanoparticles encapsulated in cages are stable and cannot agglomerate to the bulk because the cages can confine metal nanoparticles and restrict their growth. This may show great potential application in catalysis because of the high ratio of atoms remaining at the large surface area and the density of the unsaturated surface coordination sites.

Metal–organic frameworks (MOFs) have been emerging as very promising functional materials for gas storage, separation, heterogeneous catalysis, sensing, and drug delivery due to their high surface area, porosity, and chemical tunability [34–37]. These unique features make MOFs very attractive in heterogeneous catalysis. However, the catalytic active sites of most highly thermally and chemically stable MOF materials are not easily accessible for substrates due to the lack of large pores [35–37]. Development of a general and facile method of obtaining Pd NPs supported on MOFs remains challenging due to their easy agglomeration and leaching without protecting groups [37]. Inclusion of metallic nanoparticles in MOFs still remains a challenge [38–48]. So far, there are only a

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handful of MOF materials as host matrices to support metal NPs as catalysts for heterogeneous catalysis [37–53]. To the best of our knowledge, up to now, there have been no reports of employing MOFs as supports for metal NPs in dehalogenation of aryl halides.

Recently, Férey et al. introduced strong base ethylenediamine grafting onto MIL-101(Cr) ($Cr_3(F, OH)(H_2O)_2O[(O_2C)–C_6H_4–(CO_2)]_3{\cdot}nH_2O$ ($n \approx 25$) for the success of encapsulation of noble metal nanoparticles [39]. We also synthesized well-dispersed Pd nanoparticles (Pd NPs) supported on the amino-functionalized MOF MIL-53(Al)–NH_2 (Al(OH)[H_2N-BDC], H_2N-BDC = 2-aminoterephthalic acid, MIL = Materials of Institut Lavoisier) using a direct anionic exchange approach [52,53]. However, most Pd NPs remain outside of the pores of MIL-53(Al)–NH_2 due to the microporous feature that limits its application to catalysis [54]. Therefore, searching for functional mesoporous MOFs materials usable as catalysts is important. It is gratifying that Stock and co-workers have prepared amine-functionalized MIL-101(Cr)–NH_2 by postsynthetic modification of the terephthalate linker molecule through nitration and subsequent reduction with $SnCl_2$ [55]. MIL-101(Cr)–NH_2 is an excellent MOF material due to its high specific surface area, pore volume, and thermal (up to 300 °C) and chemical stability to water and common organic solvents. It has two types of mesoporous cages (2.9 and 3.4 nm) accessible through microporous windows (1.2 and 1.4 nm). The mesoporous cages can be used to confine metal nanoparticles and restrict their growth, which are pertinent to their application in heterogeneous catalysis. Furthermore, the mesoporous cages and large microporous windows may allow the large reactant molecules to reach the active site in the pores and the large product to leave from the active sites easily. Herein, we choose amino-functionalized MIL-101(Cr)–NH_2 to support Pd NPs as a highly active catalyst for the dehalogenation of aryl halides.

2. Experimental

2.1. Materials

The MOF materials MIL-101(Cr) [34], MIL-101(Cr)–NO_2 [55], MIL-101(Cr)–NH_2 [55], and MIL-53(Al)–NH_2 [54] were synthesized according to the literature. The as-synthesized MIL-101(Cr) [51] and MIL-53(Al)–NH_2 [54] were activated according to the literature. MIL-101(Cr)–NO_2:50 mg MIL-101(Cr) was added to a mixture of 4 ml concentrated sulfuric acid and 3 ml concentrated nitric acid at 0 °C. The reaction was stirred for 12 h. The mixture was allowed to warm up to room temperature and poured into 30 ml ice. The green product was filtered and washed with water. The as-synthesized product was activated subsequently using water and ethanol at 150 °C for 12 h. The resulting green solid was dried under vacuum at 70 °C for 12 h. MIL-101(Cr)–NH_2:50 mg MIL-101(Cr)–NO_2 and 2 g $SnCl_2{\cdot}2H_2O$ were suspended in 20 ml ethanol. The mixture was heated at 70 °C for 12 h. The greenish solid was centrifuged and suspended in 20 ml concentrated hydrochloric acid for 12 h to remove Sn-containing impurities. The solid was centrifuged and washed three times with water and one time with ethanol. The green solid was activated with ethanol at 80 °C for 12 h. Finally, the product was dried under vacuum at 70 °C for 12 h. All other reagents were commercially purchased and used as received.

2.2. Synthesis of Pd NPs

The activated MIL-101(Cr)–NH_2 (0.50 g, 25 ml H_2O) was treated with hydrochloric acid to pH ~4. A solution of H_2PdCl_4 (containing ca. 1.0 wt% of Pd) was added to the above acidulated slurry under vigorous agitation for 10 min. The mixture was then stirred for another 6 h. The solid was centrifuged and washed with de-ionized water and ethanol. The resulting $PdCl_4^{2-}$—MIL-101(Cr)—NH_3^+ samples (0.67 wt% Pd based on ICP-AES) were then reduced with sodium borohydride ($NaBH_4$, 0.04 g) at 273 K for 3 h to yield Pd/MIL-101(Cr)–NH_2 (0.62 wt% Pd based on ICP-AES).

2.3. Typical experimental catalysis procedure

The aryl chlorides (1 mmol) and Pd/MIL-101(Cr)–NH_2 (1 mol% Pd, 170 mg) were added to an aqueous solution of $HCOONH_4$ (10 mmol, 5 mL) under stirring at room temperature. After 3 h, the solution was centrifuged and washed three times with ethyl acetate. The organic phase was subsequently washed with water and brine and dried over Na_2SO_4. The product yield was quantified by gas chromatography (GC) analysis using *n*-dodecane as internal standard.

For the measurement of the Pd leaching during the reaction, a filtration experiment was run to investigate whether the reaction proceeded in a heterogeneous or homogeneous fashion. After 1 h, the catalyst was separated by filtration, and the filtrate was further reacted under the same conditions for another 24 h. For the recyclability test, the catalyst was recovered from each of the dehalogenation reactions of 4-chlorophenol at room temperature for 3 h, washed with water and ethanol several times, and then dried under vacuum at 50 °C for the next use.

3. Results and discussion

3.1. Preparation and characterization of Pd NPs

MIL-101(Cr)–NH_2 samples were prepared using covalent post-synthetic modification of MIL-101(Cr) with nitrating acid and $SnCl_2$ as reported by Stock et al. [55]. The nitro functionalized MIL-101(Cr)–NO_2 [55] was synthesized by nitration of blue–green MIL-101(Cr) [34] using nitrating acid (HNO_3 and H_2SO_4) for 12 h under ice cooling. Subsequently, the nitro groups were reduced to amino groups using $SnCl_2{\cdot}2H_2O$ and ethanol for 12 h at 70 °C to give green MIL-101(Cr)–NH_2. The X-ray powder diffraction (PXRD) patterns of the resulting green solids are similar to those of MIL-101(Cr) [34] (Figs. 1 and S3). The characteristic nitro and amine vibrations can be observed by IR spectroscopy. After nitration, the nitro group stretching vibration is observed at 1539 cm^{-1} (Fig. S1). Additionally, the C–N stretching vibration appears at 1168 cm^{-1}. After the reduction, the signal of the NO_2 stretching vibration is no longer present. At 3513 and 3374 cm^{-1} the asymmetric and symmetric N–H

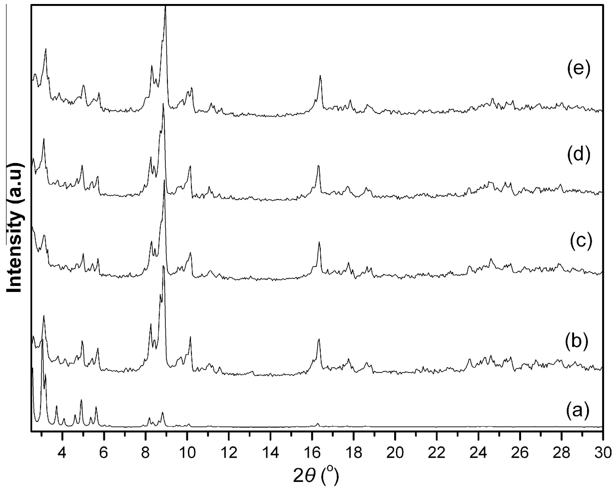


Fig. 1. Powder X-ray diffraction patterns of samples: (a) MIL-101(Cr), simulated; (b) MIL-101(Cr), activated; (c) MIL-101(Cr)–NH_2; (d) Pd/MIL-101(Cr)–NH_2, before reaction; (e) Pd/MIL-101(Cr)–NH_2, after five runs of catalysis.

Table 1
Surface area measurements for MIL-101(Cr)–NH_2 and Pd/MIL-101(Cr)–NH_2 (0.62 wt% Pd).

Sample	BET surface area (m^2 g^{-1})	Langmuir surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
MIL-101(Cr)–NO_2	1564	2379	0.82	2.09
MIL-101(Cr)–NH_2	2019.2	3297.4	1.14	2.25
Pd/MIL-101(Cr)–NH_2	1334.6	2051.8	0.74	2.21

stretching vibrations of the amino group (Fig. S1) and at 1163 cm^{-1} the C–N stretching vibration are observed [55]. The specific surface area (S_{BET} = 1564 m^2 g^{-1}, Fig. S4, Table 1) of the obtained MIL-101(Cr)–NO_2 corresponds well with that of the directly synthesized material [55]. Nitrogen adsorption measurements show lower specific surface area of the amino-functionalized porous material MIL-101(Cr)–NH_2 (S_{BET} = 2019.2 m^2 g^{-1}, Fig. 2, Table 1) than the unfunctionalized MIL-101(Cr) (S_{BET} = 3447.7 m^2 g^{-1}) because the pores were partially occupied by amino groups [52,53]. Additionally, MIL-101(Cr)–NH_2 exhibits high thermal (300 °C) and chemical stability to water and common organic solvents [55].

The successful amino modification in the cages of MOF materials has a very important consequence: the encapsulation of metals [39]. The surface amine groups of activated MIL-101(Cr)–NH_2 were neutralized with an aqueous HCl solution at the outset. Then, the chloride anions were exchanged with anionic noble metal salts $[PdCl_4]^{2-}$, and finally, the supported Pd NPs catalyst, denoted as Pd/MIL-101(Cr)–NH_2, was reduced by $NaBH_4$ at low temperature. After loading of palladium (0.62 wt% based on ICP-AES), there is no significant loss of crystallinity in X-ray diffraction patterns, and no supplementary Bragg peaks appears (but with some slight variations of the Bragg intensities), indicating that the integrity of the MIL-101(Cr)–NH_2 framework was maintained (Fig. 1) [55]. The characteristic peak of Pd (1 1 1) at $2\theta = 40.1°$ was indistinguishable due to the low Pd loading and small palladium nanoparticles [39]. The bright-field (Fig. 3) and dark-field TEM images (Fig. S5) show that most of the dispersed Pd NPs are encapsulated in the cages of the MIL-101(Cr)–NH_2, with a mean diameter of 2.49 nm, which is in agreement with the cage diameters, although some of nanoparticles still remain outside the pores. The HRTEM image (Fig. 3c) shows that small palladium particles (3 nm) have been encapsulated within the pores of MIL-101(Cr)–NH_2, while large particles with clear lattice fringes are present at the surface of the crystals. The CO pulse chemisorptions results indicate (Table S1) that the active particle diameter of Pd/MIL-101(Cr)–NH_2 is 2.8 nm, which is in agreement with the TEM results and the cage diameters. In contrast, much larger palladium particles (>20 nm) were obtained in palladium-impregnated unmodified MIL-101(Cr) under similar conditions [39], which further verified the superior effect of amine to encapsulation of noble metals. Most of Pd NPs deposited on the surface of the amine-functionalized microporous (0.86 nm) material MIL-53(Al)–NH_2 [52]. This indicates that the large mesoporous cages (2.9 and 3.4 nm) of MIL-101(Cr)–NH_2 also provide a suitable environment for dispersed nanoparticle growth. Compared with the bare MIL-101(Cr)–NH_2, Pd/MIL-101(Cr)–NH_2 exhibits a significant decrease in the N_2 amount (Fig. 2 and Table 1). The BET surface area decreases from 2019.2 to 1334.6 m^2 g^{-1} after encapsulation of Pd NPs (Table 1). The results indicate that the cavities of MIL-101(Cr)–NH_2 may be occupied by palladium NPs and/or blocked by palladium NPs that are located at the surface [38–48]. X-ray photoelectron spectroscopy (XPS) (Fig. 4) and EDS data (Fig. 3) indicate that Pd^0 and Cr^{III} coexist in the Pd/MIL-101(Cr)–NH_2 materials. In the XPS traces, the $3d^{5/2}$ and $3d^{3/2}$ peaks of Pd^0 appear at 336.7 and 341.7 eV and no obvious peak of Pd^{2+} is observed, which indicates that most of the palladium is in the reduced form [38–48].

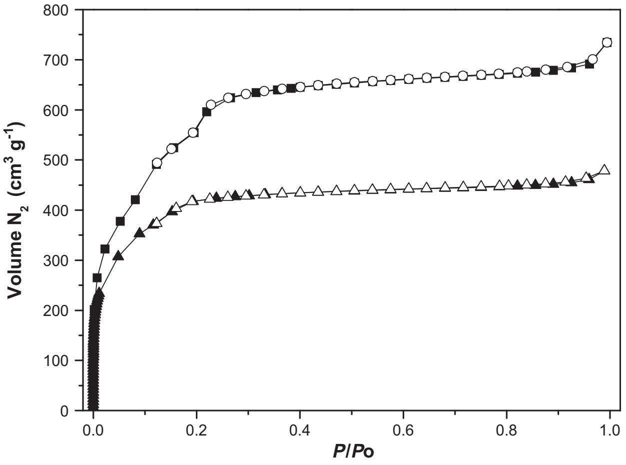


Fig. 2. Nitrogen sorption isotherms at 77.3 K for MIL-101(Cr)–NH_2 (■ = adsorption, □ = desorption) and Pd/MIL-101(Cr)–NH_2 (▲ = adsorption, △ = desorption).

3.2. Catalysis for dehalogenation of aryl chlorides

Some Pd-catalyzed dehalogenation reactions using hydrogen as a reducing agent have been reported [5,16,17,21]. However, H_2 as a gas is not always convenient to use, and relatively high pressures are generally required [21]. The use of nongaseous hydrogen sources has some advantages, because it avoids the risks and constraints associated with hydrogen gas as well as the necessity of pressure vessels and of other equipment [14]. Therefore, the aid of a stable hydrogen donor represents a useful alternative to the catalytic dehalogenation of aromatic chlorides by molecular hydrogen. Furthermore, the reported dehalogenation reactions were mostly carried out in organic solvents [6–8]. From a sustainable chemistry viewpoint, the use of water instead of volatile organic solvents is particularly important [38]. Therefore, the development of heterogeneous catalysts that can activate aryl chlorides in aqueous media is highly desirable [14].

Initially, we investigated the Pd/MIL-101(Cr)–NH_2-catalyzed dehalogenation reaction of 4-chlorophenol in water in the presence of different formic acid derivatives as hydrogen donors at room temperature (Table 2). The results show that $HCOONH_4$ (entry 3, Table 2) gives greater conversion than the other two salts tested (entries 1 and 2, Table 2) after 3 h. As shown in Table 2, the amount of catalyst is also very important for this reaction. The reaction cannot happen in the presence of only MIL-101(Cr). The use of 0.5 mol% Pd catalyst gives 76% yield of the desired product (entry 4, Table 2). It is very interesting that 4-chlorophenol can be almost completely transferred to phenol by only 1 mol% Pd catalyst (entry 3, Table 2), which is less than for the Pd/C catalyst system (5 mol% Pd) [14].

For comparison, different supported palladium catalysts have been examined under the same conditions. A commercial Pd/C catalyst (5 wt% palladium) only obtains 47% of the dehalogenation product phenol (entry 2, Table 3). Only moderate activity is also observed for our previous palladium-supported MIL-53(Al)–NH_2 (entry 3, Table 3), which exhibits high activity for the Suzuki

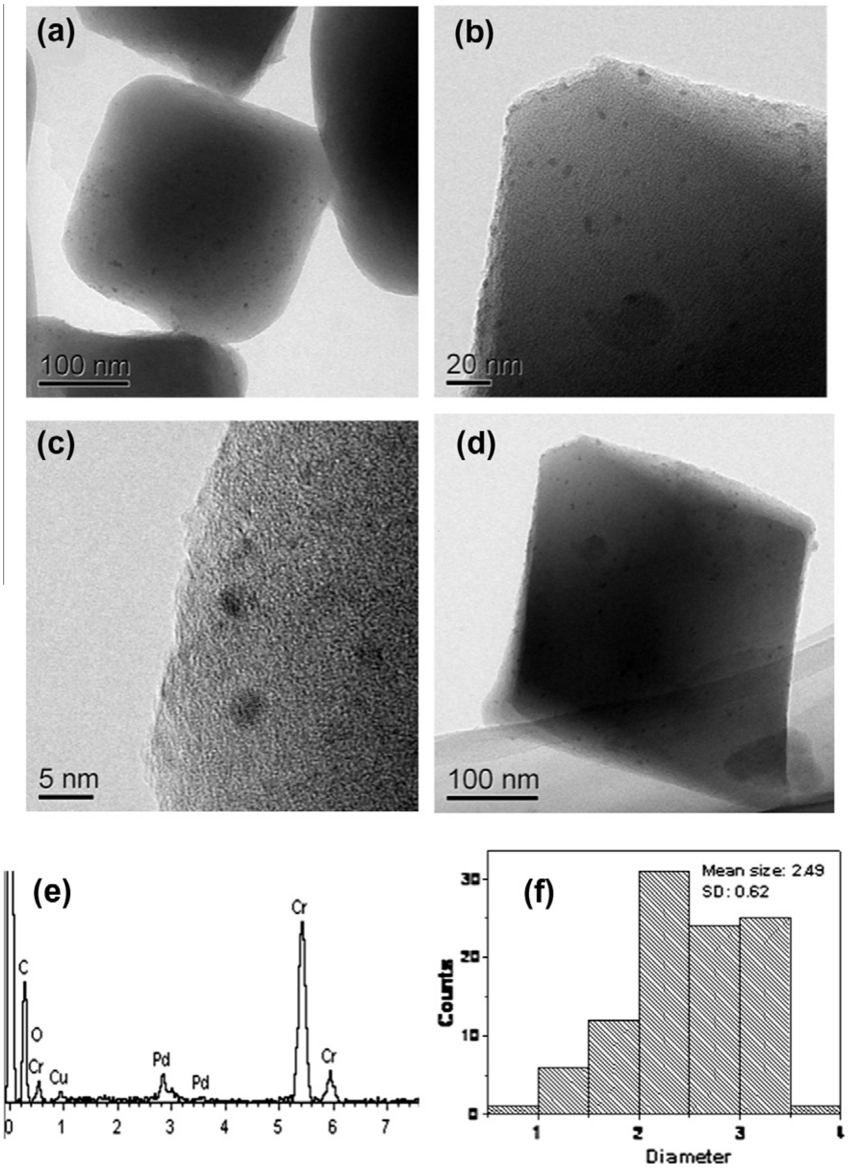


Fig. 3. Transmission electron microscopy (a and b) and high-resolution transmission electron microscopy (c) images of Pd/MIL-101(Cr)–NH_2 (0.62 wt% Pd) before the reaction and after five catalytic cycles (d), the energy-dispersive X-ray spectroscopy (EDS) pattern (e), and the size distribution of Pd NPs (f).

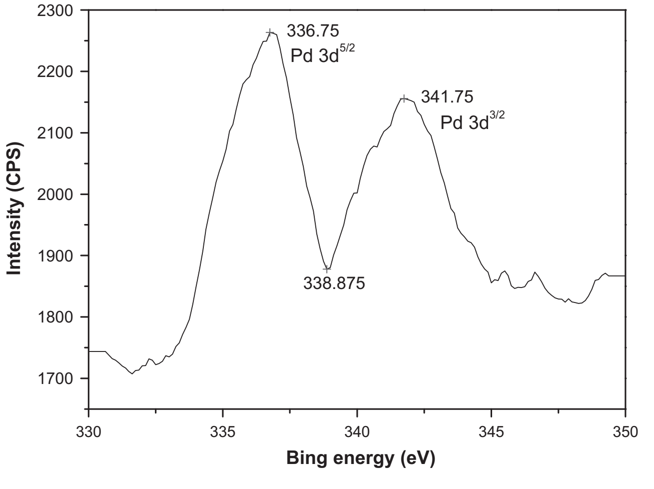
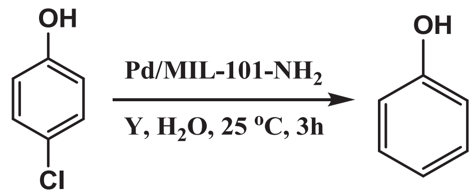


Fig. 4. XPS spectrum of a Pd/MIL-101(Cr)–NH_2 sample.

Table 2

Dehalogenation of *p*-chlorophenol in water with different hydrogen sources.[a]



Entry	Y	Yield (%)[b]
1	HCOONa	87
2	HCOOK	79
3	$HCOONH_4$	98
4[c]	$HCOONH_4$	76
5[d]	$HCOONH_4$	98
6[e]	$HCOONH_4$	0

[a] Reaction conditions: *p*-chlorophenol (1 mmol), Y (10 mmol), Pd/MIL-101–NH_2 (1 mol% Pd), H_2O (5 ml).

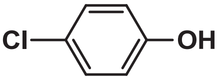
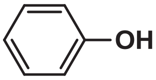
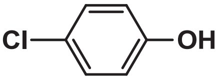
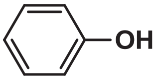
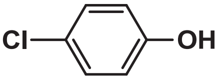
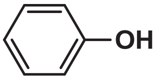
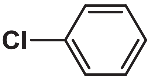
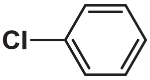
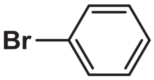
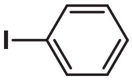
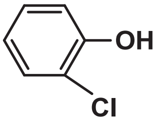
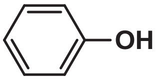
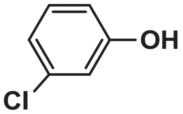
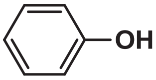
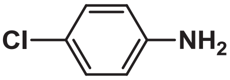
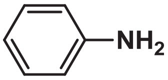
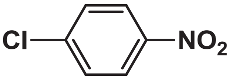
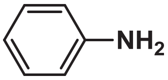
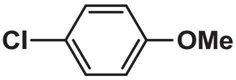
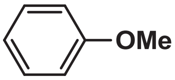
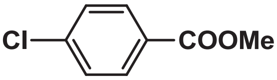
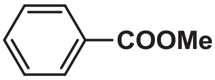
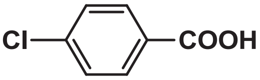
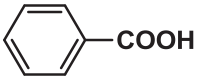
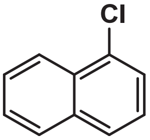
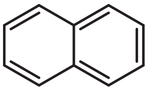
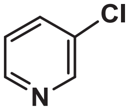
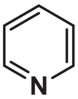
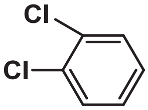
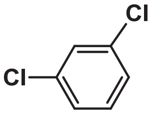
[b] GC yield.

[c] Pd/MIL-101–NH_2 (0.5 mol% Pd).

[d] Pd/MIL-101–NH_2 (2 mol% Pd).

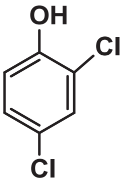
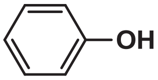
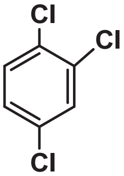
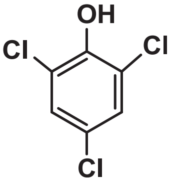
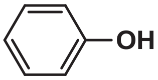
[e] MIL-101–NH_2 (0 mol% Pd).

Table 3
Dehalogenation of aryl chlorides in water with $HCOONH_4$.[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			3	98
2[c]			3	47
3[d]			3	64
4			6	92
5[e]			3	89
6			6	97
7			6	81
8			3	93
9			3	97
10			3	96
11			6	91
12			6	96
13			6	92
14			6	93
15			6	91
16			6	95
17			8	97
18			8	96
19			8	97

(continued on next page)

Table 3 (*continued*)

Entry	Substrate	Product	Time (h)	Yield (%)[b]
20			8	95
21			8	94
22			8	95

[a] Reaction conditions: aryl chloride (1 mmol), $HCOONH_4$ (10 mmol), Pd/MIL-101–NH_2 (1 mol% Pd), H_2O (5 ml), room temperature.

[b] GC yield (*n*-dodecane as internal standard).

[c] 5 wt% Pd/C (1 mol% Pd).

[d] Pd/MIL-53(Al)–NH_2 (1 mol% Pd).

[e] Tetrabutylammonium bromide (0.1 mmol) as phase-transfer agent.

reaction [52]. The high activity of Pd/MIL-101(Cr)–NH_2, as compared to Pd/MIL-53(Al)–NH_2 and Pd/C, may be ascribed to the greater surface area and accessible mesoporous cages of MIL-101(Cr)–NH_2, which may ensure the high dispersion of palladium active sites and facilitate the diffusion of reactants and large product molecules in the pores [38,51]. Moreover, it cannot be excluded that the MIL-101(Cr)–NH_2 may favor the adsorption of the aryl halide molecules and thus enhance the activity [38].

It seems that the activation of aryl chlorides is more difficult than aryl bromides or iodides due to the order of the C–X bond energy (C–Cl > C–Br > C–I) [38]. However, surprisingly, as shown in Table 3 (entries 4–7), the dehalogenation activity of the Pd/MIL-101(Cr)–NH_2 decreased in the following order: bromobenzene > chlorobenzene > iodobenzene. The phenomenon has been found in other dehalogenation systems such as liquid-phase hydrodehalogenation of halobenzenes over Pd/$AlPO_4$–SiO_2 [7,8]. The results may be the combination of two opposite factors: the carbon–halogen bond energies and the adsorption strength of the halobenzene on the catalysts [7]. Therefore, the moderate activity found for the iodobenzene could be explained as a result of its high adsorption strength over palladium catalysts [7]. It should be noted that the activation of chlorobenzene (entry 4, Table 3) needs a longer time than that of 4-chlorophenol due to its being insoluble in water. Interestingly, the addition of the phase-transfer agent tetrabutylammonium bromide enhanced the dehalogenation rate significantly (entry 5, Table 3).

We next examined the scope of the reactions with a variety of substituted aryl chloride molecules (Table 3). The hydroxyl groups ortho and meta to chlorine are also well tolerated in the reactions (entries 8 and 9, Table 3). Interestingly, the dehalogenation reactions proceed extraordinarily well with a variety of substituted chlorobenzenes bearing electron-withdrawing and electron-donating groups, giving the corresponding aromatic products (entries 10–14, Table 3). It should be noted that 4-chloronitrobenzene was almost fully transferred to aniline, which was accompanied by the reduction of the nitro group in the course of the dehalogenation reaction (entry 11, Table 3). Additionally, the halogenated condensed ring and heterocyclic aromatic hydrocarbons, such as α-chloronaphthalene and 3-chloropyridine, could also be dehalogenated with very high activities (entries 15 and 16, Table 3). Most polychlorinated benzenes are priority pollutants [2]. Interestingly, water is used as solvent, and the dichlorobenzene derivatives (1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 2,4-dichlorophenol) and trichlorobenzene derivatives (1,2,4-trichlorobenzene and 2,4,6-trichlorophenol), which are not soluble in water, can be dehalogenated completely with high activity in only 8 h (entries 17–22). Interesting, there was no chlorobenzene or chlorobenzene derivatives. Notably, almost no biphenyls, cyclohexane, cyclohexanone, and cyclohexanol were found in the above reactions. The inorganic–organic hybrid material MIL-101(Cr)–NH_2 with large specific surface area and windows and mesoporous cages favor the adsorption of the aryl halide molecules, which was responsible for the high dehalogenation [38].

It is very important whether the chromium leaches to the solution from the support. After the catalysis workup, there is no detectable leaching of chromium to solution because of the high-stability MIL-101(Cr)–NH_2 (Cr < 0.1 ppm for drinking water) [56], so the support will not contaminate the environment. Furthermore, Cr(III) compounds are neither irritating, mutagenic, nor carcinogenic [56]. All these properties make MIL-101(Cr)–NH_2-based materials attractive for catalysis.

It is well known that one of the disadvantages of the supported Pd catalyst is the leaching of palladium into the solution, resulting in loss of the activity of the supported Pd catalysts [51]. For these reasons, leaching of the metal from the Pd/MIL-101(Cr)–NH_2 catalyst has been examined. After the workup, ICP-AES analysis shows that the amount of Pd leaching into the reaction mixture is very low (0.5 ppm). The result may be attributed to the difficulty of escape from the mesoporous cages (2.9 and 3.4 nm) through microporous windows (1.2 and 1.4 nm) for the nanoparticles. If the catalyst was removed after 30% conversion (after 1 h) and the resulting filtrate was monitored under identical reaction condition for another 24 h, no further conversion was detected. These results suggested that the reaction may proceed over the Pd catalyst surface in a heterogeneous fashion [38–48]. The advantages of the Pd/MIL-101(Cr)–NH_2 catalyst are that the catalytic reactions can be

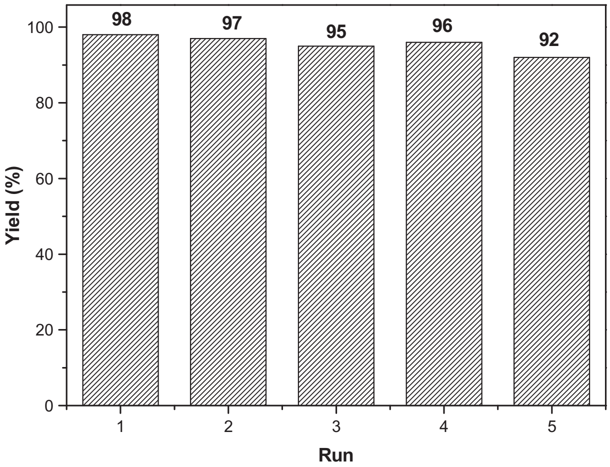


Fig. 5. Recycling of Pd/MIL-101(Cr)–NH$_2$ for five runs of the dehalogenation of 4-chlorophenol at room temperature for 3 h.

conveniently carried out in air and that the separation of the catalyst can be achieved easily by centrifugation. After being recycled for five runs of the dehalogenation reaction of 4-chlorophenol, the Pd catalyst still exhibits remarkable activity (the yield decreased only 6%) (Fig. 5). The PXRD study shows that the crystalline structure of the catalyst is mostly retained after five catalytic cycles (Fig. 1). The TEM image of the reused catalyst reveals that the Pd NPs size is very similar to the initial material (Fig. 3). This may be ascribed to confinement of the Pd NPs in mesoporous cages and thus restriction of their growth. These results indicate that the reaction proceeds in a heterogeneous fashion [38–48].

4. Conclusions

In summary, highly dispersed Pd NPs encapsulated in amine-functionalized mesoporous MOFs MIL-101(Cr)–NH$_2$ have been prepared easily with the help of NaBH$_4$ under mild conditions. The well-dispersed Pd NPs confined in mesoporous cages showed high activity for dehalogenation of aryl chlorides in water under mild conditions. Furthermore, the catalyst is easily recoverable and can be reused several times without leaching or loss of activity.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.05.003.

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