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Palladium Nanoparticles Supported on Mixed-Linker Metal–Organic Frameworks as Highly Active Catalysts for Heck Reactions

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Well-dispersed palladium nanoparticles (Pd NPs) supported on amine-functionalized, mixed-linker metal–organic frameworks (MIXMOFs) based on MIL-53(Al) were prepared by using the ion-exchange method. Pd NPs were characterized by powder X-ray diffraction (XRD), N₂ adsorption, transmission electron microscopy (TEM), inductively coupled plasma atomic emission

Introduction

The palladium-catalyzed Heck reaction between aryl halides and olefins is one of the most important reactions for the formation of carbon-carbon bond in synthetic organic chemistry.^[1] In traditional Heck reactions, with palladium salts or organometallic complexes with special ligands (such as phosphines) that are sensitive to moisture and air, are generally used,^[1] and the homogeneous systems often suffer difficulty in separation and recycling of expensive Pd catalyst.^[2] Therefore, it is desirable to develop heterogeneous catalysts for Heck reactions to overcome such problems.^[3] Heterogeneous catalysts are distinguished from homogeneous catalysts in the industrial application for their advantages of easy of separation of product and the recovery of expensive catalyst. However, Pd NPsan important kind of heterogeneous catalysts-are prone to aggregate and lose their catalytic activity without the use of a stabilizer.^[4] Therefore, they need to be supported on solid materials (such as carbon frameworks, zeolites, silica, polymers, Al₂O₃) to be useful as catalyst for Heck reactions.^[1-14] In addition, in many cases, the catalytic active sites may be lost due to the leaching of palladium in supported systems which makes the catalyst difficult to recovered and reused.^[3] Therefore, a suitable supports for Pd NP catalysts are important for heterogeneous catalysis.

Metal–organic frameworks (MOFs) have emerged as very promising functional materials for gas storage, separation, heterogeneous catalysis, sensing, and drug delivery because of their high surface area, porosity, and chemical tunability.^[15–25] Although there are several approaches that are used to load Pd NPs onto porous MOFs by solution infiltration and surface grafting methods,^[25–29] developing a general and facile method to incorporate active Pd NPs on MOFs remains a challenge owing to the easy agglomeration and leaching into solution without the need for protecting groups.^[25] Thus, there are a limited number of Pd NPs supported on MOFs and even fewer of them can act as catalysts for heterogeneous cataly-sis.^[15,17,25,30–33]

spectroscopy (ICP-AES), and X-ray photoelectron spectroscopy (XPS). The mean diameter of Pd NPs is approximately 3.2 nm. It was found that the Pd NPs supported on amine-functionalized MIXMOFs are stable at high temperature. The Pd NPs exhibit efficient catalytic activity for Heck reaction and can be easily recovered and reused.

Recently, mixed-linker metal-organic frameworks (MIXMOFs), which incorporate different functionalities on linking groups by the mixing linkers, have attracted substantial attention.^[34-42] The MIXMOFs would constitute new materials that contain a tunable number of functional sites and would inevitably lead to a complex chemical environment.^[34] Therefore, they may provide opportunities for the preparation of materials with unusual properties, such as thermal stability, gas adsorption, and catalysis.^[34-42] MIL-53(AI) (AI(OH)[O₂C-C₆H₄-CO₂]) is one of the most outstanding materials that has been extensively used in gas storage and separation science.^[43-46] Amine-functionalized MIL-53(Al)-NH₂ (Al(OH)[H₂N-BDC], where H_2N -BDC = 2-aminoterephthalic acid), is an MIL-53(AI) analogue that contains free amine group.^[25,47-51] It not only drastically enhances the affinity for CO2 and basic catalysis, but can also be used for postmodification of amine groups with a set of cyclic anhydrides.^[49] Recently, Kleist, Baiker, and co-workers reported that amine-functionalized, mix-linker MIL-53(Al) materials exhibit higher thermostability than MIL-53(AI)-NH2.[40-41] As an extension of our previous work on the preparation of Pd NPs supported on amine-functionalized MIL-53(Al)-NH₂ and their application in Suzuki-Miyaura cross-coupling reactions,^[52] herein we will report the facile preparation of highly active and stable Pd NPs supported on amine-functionalized, mix-linker MIL-53(Al) materials and their application in Heck reactions.

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Results and Discussion

Preparation and characterization of Pd NPs supported on MIXMOFs

Compared with MIL-53(Al)-NH₂, MIXMOFs **1**, **2**, and **3** (Scheme 1) are more stable and economical to synthesize owing to the use of cheap terephthalic acid.^[41] Powder X-ray



Scheme 1. Synthesis of MIXMOFs 1 (x=0.1), 2 (x=0.5), and 3 (x=0.9) based on MIL-53(Al). BDC = benzene-1,4-dicarboxylate, ABDC = 2-aminobenzene-1,4-dicarboxylate.

diffraction (XRD) studies indicate that all three compounds are highly crystalline and of the same structures as in MIL-53(AI) and MIL-53(AI)-NH₂ (Figure 1).^[41,44,49] Nitrogen sorption studies show that the Brunauer–Emmett–Teller (BET) surface area of MIL-53(AI) (928 m²g⁻¹) and MIL-53(AI)-NH₂ (654 m²g⁻¹) are lower than that of **2** (997 m²g⁻¹; Figure 2). The results demonstrate that the properties of MIXMOFs are not simple linear sums of those of the pure components, and thus support the notion that the sequence of functionalities within MIXMOFs can enhance a specific property.^[34]

The high surface area, porous structure, and stability in water and common organic solvent make the amine-functionalized MIXMOFs attractive catalyst supports. Recently, Férey and co-workers reported an anion-exchange method for the encapsulation of noble metals over the ethylenediaminegrafted MIL-101(Cr) (Cr₃(F,OH)(H₂O)₂O[(O₂C)-C₆H₄-(CO₂)]₃·nH₂O ($n\approx$ 25)).^[29] However, it is difficult to control the concentration



Figure 1. Powder XRD patterns of the MIL-53(Al), 1, 2, 3, and MIL-53(Al)-NH₂.



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Figure 2. Nitrogen sorption isotherms of MIL-53(AI), MIXMOFs 2, Pd/2, and MIL-53(AI)-NH $_{2}$.

of the strong base ethylenediamine; an excess amount of strong base may destroy the frameworks. Meanwhile the amine-functionalized MIXMOFs based on MIL-53(AI) can be obtained directly by replacing terephthalic acid with aminoterephthalic acid, and thus avoids introducing the strong base ethylenediamine to the MOFs. Herein, we use the ion-exchange approach for preparation of Pd NPs supported on amine-functionalized MIXMOFs based on MIL-53(AI). The surface amine groups of **1**, **2**, and **3** (see the Experimental Section for details) were first neutralized by aqueous HCl, followed by ionic reactions of the positively charged ammonium groups on the surface with anionic noble metal salts $[PdCl_4]^{2-.[25b,29,52]}$ Finally, the obtained material containing palladium salts were reduced with NaBH₄ at low temperature.

After the loading of palladium, there is no apparent loss of crystallinity according to X-ray diffraction patterns, thus indicating that the framework of **2** is well maintained (Figure 3).^[52]

The characteristic peak of Pd (111) at $2\theta = 40.1^{\circ}$ is indistinguishable owing to the low Pd loading and small diameter Pd NPs.^[15] The Pd/2 exhibits a diminished BET surface area of 982 m²g⁻¹, whereas that of MIXMOFs 2 is 997 m²g⁻¹ (Figure 2). The decrease of surface area indicates that the cavities of 2 may be occupied and/or blocked by the palladium NPs located at the surface.^[15] The TEM images of Pd/2 (Figure 4) show that the Pd NPs are well dispersed on the outer surface of the support and no aggregation is observed, which are similar to the Pd NPs supported on MIL-53(AI)-NH2^[52] and MOF-5.^[15] The mean diameter of Pd NPs is approximately 3.2 nm (Figure 4), meanwhile the palladium nanoparticles supported on the amino-free MIL-53(AI) aggregate immediately.^[52] The presence of amino group on the functionalized linker has been proven to be beneficial for the stabilization of Pd species.^[39] It may not be precluded that there exists coordination interactions between palladium nanoparticles and amino groups. X-ray energy-



Figure 3. Powder XRD patterns of the MIXMOF 2 containing 50% of ABDC, Pd/2, and Pd/2 after 5th cycle.



Figure 5. XPS measurement of Pd/2 (0.96 wt% of Pd).

dispersive spectroscopy (EDS) further confirm the presence of the Pd in the Pd/**2** samples (Figure 4). In the X-ray photoelectron spectroscopy (XPS) trace (Figure 5), the $3d^{5/2}$ and $3d^{3/2}$

peaks of Pd^0 appear at 336.0 and 341.3 eV, respectively, and no obvious peak of Pd^{2+} is observed, thus indicating that palladium is in the reduced form.^[30]



Heck reactions catalyzed by Pd NPs

The Heck reactions were first performed using a low amount of palladium (a molar ratio: aryl halide/Pd = 2000) and an excess of olefin with respect to aryl halide (molar ratio = 1.5) to avoid of the formation of homocoupling by-products.^[3] Pure coupling products were obtained by column chromatography and characterized by NMR spectroscopy. The compounds were selectively obtained with *trans* configuration.

Initially, we used Pd/MIL-53(AI)-NH2^[52] to investigate the effects of base and solvent for the Heck reaction of brombenzene and styrene at 120°C (Table 1). The results showed that organic base triethylamine gave higher yields than that of inorganic bases such as Na₂CO₃, K₃PO₄, and NaOAc (Table 1, entries 1-4). No product was obtained in the absence of the base (Table 1, entry 5). The solvent also had a significant influence on the catalyst activity. Compared with NMP and





o-xylene (Table 1, entries 6 and 7), higher TOF ((mol of prod) per (mol of Pd per hour)) was obtained in DMF (Table 1, entry 4). It was noted that no Pd black was observed under such rigorous conditions during the reaction. Therefore, the amino-stabilized Pd NPs are air-stable up to 120°C and their catalytic activity is virtually independent of the presence of air. The amount of catalyst is also very important for the reaction. The reaction could not happen in the presence of only MIL-53(Al)-NH₂. Although the use of 0.005 mol% and 0.01 mol% of Pd catalyst gave higher TOF, it gave only 28% (Table 1, entry 10) and 59% (Table 1, entry 9) yield of the desired products, respectively. It is very interesting that the bromobenzene can be activated effectively by only 0.05 mol% of Pd catalyst and very high yield was obtained (81%; Table 1, entry 4). The product yield was only 83% upon increasing the Pd catalyst to 0.1 mol% (Table 1, entry 11).

Because the type of support is important for Pd NPs catalysis, Pd NPs supported on different supports (MIL-53(AI), 1, 2, and 3) as well as commercially available Pd/C were used in Heck reactions (Table 2). Notably, no product was obtained without the use of Pd catalyst (Table 2, entry 7). The Pd NPs supported on amine-functionalized MOFs (1, 2, 3, and MIL-53(Al)-NH₂) showed significantly higher reactivity (up to 76% yield for the brombenzene substrates) than that of Pd/MIL-53(Al) and Pd/C. These results might be attributed to the Pd NPs agglomeration (Figure S1).^[29] Interestingly, the different amount of amines in the supports also affected the activity of the Pd catalyst. By increasing of the amount of the amine groups, the activity of the catalyst increases first (up to 93% yield with Pd/2, 50% NH₂; Table 2, entry 3), and then declines (81% yield with MIL-53(Al)-NH₂; Table 2, entry 5). It may not preclude that there exists coordination interactions between palladium and amino groups.^[39,52] A certain number of amino



groups on the functionalized linker proved to be beneficial for the immobilization of Pd species, which prevent the agglomeration of Pd NPs. However, the strong interaction between the excess amine groups and Pd species may lead to weakening of the palladium activation for the substrate.^[53,54] It may be that the presence of distinct sequences of functionalities in the MIXMOFs leads to a complex chemical environment for catalysis.^[34]

Next, Pd/2 as the most efficient catalyst was applied to examine the scope of different substrates in the Heck reaction. A variety of aryl halides were coupled with different olefins in the presence of Pd at low loading (0.05 mol% of Pd)^[6] under the optimized reaction conditions (Table 3). The Heck reaction of styrene with iodobenzene proceeded easily at 120°C resulting in trans-stilbene in excellent yields after 30 minutes. Owing to the higher bond energy of the C-Br and C-Cl bonds, aryl bromide and chlorobenzene compounds are difficult to activate. Therefore, the reactions of aryl bromides (or chlorobenzene) with different olefins required harsh conditions and extended reaction times. Interestingly, as seen from Table 3, the Heck reactions of a variety of aryl bromide derivatives with styrene could also proceeded smoothly at 120°C and gave the corresponding products in high yields after 6 h (Table 3, entries 2, 7-13). The electron-withdrawing groups (-NO₂, -CN, -CF₃, and -COCH₃) in the para position relative to bromine can weaken the C-Br bond,^[3] so these substituted bromobenzene compounds reacted more rapidly than bromobenzene (Table 3, entries 7-10). Reactions between styrene and a variety of electron-rich substrates such as 4-methy- and 4-methoxyl-substituted aryl bromides, also proceeded smoothly and gave the coupling products in good yields (Table 3, entries 11 and 12). Notably, the electron-donating and sterically hindered 2-methoxyl-substituted bromobenzene also gave good yields (Table 3, entry 13). However, the most challenging, yet readily accessible, chlorobenzene had much lower reactivity even after 24 hours (Table 3, entry 3). In addition, various olefin derivatives with different ester substituents were applied to this

Table 3. Results for the Heck reaction catalyzed by Pd/2. ^[a]					
$\begin{array}{ c c c c c c } \hline & & & & \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ R^1 \end{array} \xrightarrow{\begin{tabular}{ll} A & A & A \\ \hline & & & \\ R^2 & \hline & & \\ \hline & & & \\ R^2 & \hline & & \\ \hline & & & \\ R^2 & \hline & & \\ \hline & & & \\ R^2 & \hline & & \\ \hline & & & \\ R^2 & \hline & & \\ R^2 & \hline & & \\ \hline & & & \\ R^2 & \hline \\ R^2 & \hline & \\ R^2 & \hline \\ R^2$					
Entry	R ¹	Х	R ²	Yield [%] ^[b]	TOF [h ⁻¹]
1 ^[c]	H	-	Ph	97	3880
2	Н	Br	Ph	93	310
3 ^[d]	Н	Cl	Ph	11	9
4	Н	Br	CO₂CH ₃	95	317
5	Н	Br	CO₂ <i>n</i> Bu	94	313
6	н	Br	CO₂tBu	91	303
7	4-NO ₂	Br	Ph	98	327
8	4-CN	Br	Ph	97	323
9	4-CF ₃	Br	Ph	95	317
10	4-COCH ₃	Br	Ph	96	320
11	4-Me	Br	Ph	86	287
12	4-OMe	Br	Ph	81	270
13	2-OMe	Br	Ph	66	220
14 ^[e]	Н	Br	Ph	65 (67) ^[f]	216
15 ^[g]	н	Br	Ph	92	306
[a] Reaction conditions: aryl halide (1 mmol), olefin (1.5 mmol), Pd/MIX-MIL-53(Al) and 50% of NH ₂ (0.05 mol% of Pd), NEt ₃ (1.5 mmol), DMF (3 mL), 6 h. [b] Yield of isolated product. [c] 30 min. [d] 24 h, yield base on GC analysis. [e] The catalyst was removed after 3 h. [f] The filtrate was kept string for 24 h. [d] After being stored in air for theorem.					

reaction (Table 3, entries 4–6). It was found that the cross-coupling of bromobenzene with these ester-substituted olefins afforded the corresponding *trans*-configured products in excellent yields. Interestingly, the efficiency of the *tert*-butyl acetatesubstituted olefin was not affected by its steric hindrance and gave high yield (Table 3, entry 6).

Notably, one of the disadvantages related to the use of supported Pd catalysts in the Heck reaction is leaching of the palladium into the solution, and results in contamination of the product with metal that is difficult to remove along with loss of the expensive Pd catalyst.^[3–5,55] Therefore, the leaching of the metal from Pd/**2** catalyst was examined. After the workup, inductively coupled plasma (ICP) analysis showed that the amount of Pd leached into the reaction mixture was very low (0.1 ppm). Pleasingly, the low amount of Pd satisfies specifications required by the pharmaceutical industry regarding the final purity of the products (Pd < 2 ppm).^[3] A hot-filtration experiment clearly indicated that the reaction stopped when the filtrate was further subjected to the same reaction (Table 3, entry 14).

Advantages of the Pd/2 material were that the catalytic reactions could be conveniently carried out in air, and the separation of this heterogeneous catalyst could be achieved easily by filtration. Less active 4-methoxy-1-bromobenzene and styrene were used for reusability experiments. The results indicate that after being recycled for five runs, the Pd catalyst still showed a remarkable activity (a reduction from 81% to 76% yield; Table 4). The TEM image of the reused catalyst (Figure 5) reveals that the mean diameter of the nanoparticles is 3.4 nm, which is very similar to that before the catalysis reaction. The results illustrate that the loss of palladium active sites is negli-



gible, thus resulting in the preservation of catalytic activity.^[30] Moreover, the Pd catalysts supported on amine-functionalized MOFs was comparably active after being stored in air for three months (Table 3, entry 15). These features are obvious improvements from existing air- and moisture-sensitive homogeneous palladium-phosphine catalysts.^[10]

Conclusion

In conclusion, amine-functionalized MIXMOFs based on MIL-53(Al) drastically enhance N₂ adsorption, thus suggesting that the properties of MIXMOFs are not simple linear sums of those of the pure components. Moreover, we have developed a facile approach for the preparation of Pd NPs catalysts supported on amine-functionalized MIXMOFs based on MIL-53(Al). These well-dispersed Pd NPs show high activity and selectivity for Heck reactions. The Pd NPs catalysts exhibit high stability which can be recycled and reused easily.

Experimental Section

MIL-53(AI),^[44] MIL-53(AI)-NH₂,^[49,50] and amine-functionalized MIX-MOFs AI(OH)(BDC)_{1-x}(ABDC)_x based on MIL-53(AI) (BDC = benzene-1,4-dicarboxylate, ABDC = 2-aminobenzene-1,4-dicarboxylate, x = 0.1; 0.5; 0.9, denoted **1**, **2**, **3**, respectively; Scheme 1) were synthesized according to literature procedures.^[40] The as-synthesized MIL-53(AI) was treated at 330 °C for 12 h to remove unreacted terephthalic acid. The obtained MIXMOFs and MIL-53(AI)-NH₂ were washed with DMF, and subsequently soaked in methanol at 70 °C for 24 h. The solid was finally dried overnight at 130 °C under vacuum. All other reagents were commercial available and used as received.

The activated MOFs MIL-53(Al)-NH₂, **1**, **2**, and **3** (0.50 g) in H₂O (40 mL) were treated with hydrochloric acid to give a pH value of 4. Then the solution of H₂PdCl₄ (containing 1.0 wt% of Pd) was added drop-wise to the above acidulated solution under vigorous stirring for 10 min and then stirring for 8 h. The resulting solid was centrifuged and washed with deionized water and ethanol. The samples were reduced by NaBH₄ (0.04 g) at 273 K for 3 h to obtain Pd NPs (denoted Pd/MIL-53(Al)-NH₂, Pd/1, Pd/2, and Pd/3). For comparison, a solution of H₂PdCl₄ (containing ca. 1.0 wt% of Pd) was added to the activated MIL-53(Al) (0.50 g) which was suspend-

ed in H₂O (40 mL) under vigorous agitation for 10 min and the mixture was then stirred for 24 h. The solid was centrifuged and washed with deionized water and ethanol. The resulting MIL-53(AI) samples containing palladium salts were then reduced with NaBH₄ (0.04 g) at 273 K for 3 h to obtain Pd/MIL-53(AI) (0.19 wt% of Pd based on ICP-AES).

Powder XRD patterns were recorded on a Rigaku-Dmax2500 diffractometer equipped with CuK α radiation ($\lambda = 0.154$ nm). Analysis of the noble metal content was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). The morphologies of the catalysts were studied using a JEOL-2010 transmission electron microscope (TEM) working at 200 KV. The samples were prepared by placing a drop of product in ethanol onto a continuous carbon-coated copper TEM grid. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10–9 Torr. The NMR spectra were measured on an AVANCE III Bruker Biospin Corporation Spectrometer. The GC-MS measurements were performed on a Varian 450-GC/240-MS.

Typically, aryl halide (1 mmol), vinyl substrate (1.5 mmol), NEt₃ (1.5 mmol), and palladium catalyst (0.05 mol% of Pd) were added to DMF (3 mL). The reaction mixture was stirred at 120 °C for 0.5–24 h. After the reaction was complete, the solution was centrifuged and washed with ethyl acetate three times. The organic phase was subsequently washed with water, brine, dried over Na₂SO₄, and concentrated in vacuo. The crude residue was quantified by GC-MS analysis. The product was purified by column chromatography on silica gel (mixture of light petroleum and ethyl acetate as the eluent). The identification of the products was conducted by ¹H NMR and ¹³C NMR measurement.

For the measurement of the Pd leaching during the reaction, the mixture was hot-filtrated under vacuum. The solid was washed with water (5 mL) and ethanol (5 mL), and the liquid phase was analyzed by ICP-AES. Moreover, a hot-filtration experiment was also run to investigate if the reaction proceeded in a heterogeneous or homogeneous fashion. After 3 h, the catalyst was separated by hot-filtration and the filtrate was further subjected to the same reaction conditions for 24 h. For the recyclability test, the catalyst was recovered from the mixture after each reaction, washed with water and ethanol, and then dried for the next run.

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