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Short communication

Palladium nanoparticles encapsulated in MIL-101-NH₂ catalyzed one-pot reaction of Suzuki-Knoevenagel reaction



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G R A P H I C A L A B S T R A C T

In this paper, Pd@MIL-101-NH₂ were synthesized, which was used as heterogeneous catalysts for one-pot Suzuki-Knoevenagel reactions. As expected that Pd@MIL-101-NH₂ exhibited remarkably catalytic activity and selectivity. Moreover, other reaction conditions have also been explored involving solvents, reaction temperatures and other catalysts for the sake of achieving the best catalytic efficiency.



ARTICLE INFO

Keywords: Palladium MIL-101-NH₂ Suzuki Knoevenagel One-pot ABSTRACT

Bifunctional Cr-MOF catalysts containing palladium nanoparticles (NPs) have been prepared. Combining the high activity of Pd NPs and base sites in MIL-101-NH₂, the catalysts (Pd@MIL-101-NH₂) exhibited distinct catalytic activity in a one-pot Suzuki-Knoevenagel reaction. Pd@MIL-101-NH₂ has been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and fourier transform infrared spectroscopy (FT-IR). Various substituted phenylboronic acids were used to research the one-pot reaction. The results were highly satisfactory, not only got high yield, but reduced reaction time. Leakage experiments further demonstrated that there is no leaching of active palladium nanoparticles during the reactions. Catalysts could be reused for at least five cycles and activity is not significantly decreased.

The Suzuki cross-coupling reaction is one of the most effective methods for forming a C–C bond and engendering asymmetric biaryl groups [1–3]. In the past few decades, this reaction has been industrially applied to the production of compounds such as biaryl and alkene derivatives. Recently, this reaction has been succeeded in compounding natural products [4–6], drugs [7–9] and conducting polymers [10,11]. Knoevenagel condensation reactions are a process for

production of α,β -unsaturated carbonyl compounds which are widely used in the synthesis of chemicals [12], biologicals [13,14], and pharmaceuticals [15,16]. In general, Knoevenagel condensation reaction was catalyzed by homogeneous catalysts, which have the disadvantage that catalysts cannot be recycled. Therefore, it is quite desirable to develop heterogeneous catalysts that achieve those reactions from an environmental and economic standpoint. Compared with traditional

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step-by-step reactions, one-pot [17–22] reactions have obvious advantages, such as less production waste, less energy consumption, shorter reaction time and more environmental protection.

Metal-organic frameworks (MOFs) [23-26] are composed of metal clusters or ions and organic ligands. Owing to their adjustable high pore structure and large specific surface areas, they have extensive application fields, such as catalysis [27-36], gas storage [37], adsorption [38], biomedicine [39,40]. For decades, MOFs have proved their enormous potentiality as heterogeneous catalysts, especially as a support carrier for metal nanoparticles. Although plenty of researches have been conducted on the role of MOFs in catalysis, the number of studies on bifunctional metal nanoparticles@MOFs for catalvzed one pot reactions is limited. Although single-step reactions have been reported in the literature, the use of bifunctional MOFs to simultaneously catalyze the Suzuki-knoevenagel one-pot reaction has hardly been reported, so there is no suitable catalyst to compare. It is worth mentioning that metal nanoparticles@MOFs catalysts have many advantages than homogeneous catalysts, such as reuse and separate. Moreover, compared with nanoparticles, metal nanoparticles@MOFs catalysts have good stability and not easy to be aggregated. Here, we developed a bifunctional one-pot heterogeneous catalysts by encapsulating Pd nanoparticles (NPs) into cavities of MIL-101-NH₂. They can catalyze Suzuki cross-coupling reaction of aldehydes and subsequent Knoevenagel condensation reaction of malononitrile. For all we know, this is the first example of applying MOF-based heterogeneous catalysts to a one-pot Suzuki-Knoevenagel reactions. Additionally, and they can be reused multiple times without distinct catalytic activity.

The X-ray powder diffraction measurements of samples were detected by Bruker AXS D8 advanced automated diffractometer with Cu- $K\alpha$ radiation. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded with the Nicolet 5DX spectrometer in range 4000–400 cm⁻¹ using KBr pellets. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyrisl (25–800 °C, 5 °C min⁻¹, flowing N₂). Transmission electron microscopy (TEM) graphics of samples was acquired on JEOL-2010 electron microscope with an operating voltage of 200 kV. Energy-dispersive X-ray (EDX) spectra were collected at a field-emission instrument of the type SU8010. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) quantified the content of Pd in Pd@MIL-101-NH2. Gas absorption isotherms were performed with a Belsorp-Max automatic volumetric adsorption apparatus. The catalytic reaction products were analyzed and identified by SP-2100A gas chromatograph (GC, equipped with a Kromat-Bond Series capillary column and a flame ionization detector).

In order to confirm the successful synthesis of MIL-101-NH₂ and Pd@MIL-101-NH₂, TEM, XRD, EDX, ICP-AES and FT-IR characterizations were performed. XRD of MIL-101-NH2 and Pd@MIL-101-NH2 is displayed in Fig. 1, the XRD pattern of as-synthesized MIL-101-NH₂ matched well with the already published XRD patterns, which suggest that MIL-101-NH₂ was obtained. After loading of Pd NPs, there was no apparent loss of crystallinity in XRD patterns (Fig. 1), which demonstrated that the frameworks of MIL-101-NH₂ are mostly maintained. Furthermore, we did not find any X-ray diffraction peaks from Pd nanoparticles, probably due to the low Pd content. The FT-IR spectrums of as-synthesized samples with a spectral range of $400-4000 \text{ cm}^{-1}$ were illustrated in Fig. S1. Strong bands exhibited by MIL-101-NH₂ in the range of 1750–1300 cm⁻¹ were COO⁻ symmetric, asymmetric stretching vibration, C-C stretching vibration, which proved the existence of carboxylate linker in MIL-101-NH₂ [41]. The C-H in-plane and out-of-plane bending vibration of the aromatic ring corresponds to a weak peak at 973 cm^{-1} and a peak at 759 cm^{-1} [42]. In addition, a clear peak at 1619 cm⁻¹ was N-H bending vibration, and N-H asymmetric and symmetric stretching vibration of the amino groups correspond to weak double peaks at 3378 cm^{-1} and 3461 cm^{-1} [43]. All of peaks of MIL-101-NH₂ can be found correspondingly in spectrum of Pd@MIL-101-NH2. The above evidence demonstrated that the structure of MOF remained intact after attached Pd NPs, which was



Fig. 1. PXRD patterns of simulated (black), MIL-101-NH₂ (red), Pd@MIL-101-NH₂ (blue), recovered after five runs (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

consistent with the XRD result. TEM images illustrated that Pd nanoparticles were adequately dispersed into MIL-101-NH₂ (Fig. 2a), which increased activity of the catalyst. It can be found in Fig. 2b that it has a uniform size of 1.5 ± 1 nm. Energy-dispersive X-ray spectroscopy (EDX) analysis showed a pattern containing element of Pd (Fig. 2a). The content of Pd which was determined by ICP-AES was 2.02 wt%. To reveal thermal stability of Pd@MIL-101-NH2. Thermogravimetric Analysis (TGA) experiment was carried out under N₂ atmosphere conditions at a rate of 10 °C min⁻¹ over a range of 25–800 °C. As illustrated in Fig. S2, the first main weight-loss was due to decomposition of the solvent molecule DMF, unreacted 2-aminoterephthalic acid in cage of MOF to ca. 100 °C. Weight losses in 393 °C attributed to decomposition of organic skeleton. This decomposition temperature compared well to the value reported in the literature [44]. BET surface areas of MIL-101-NH₂ and Pd@MIL-101-NH2 were determined by N2 physisorption measurements at 77 K (Fig. S3). The BET surface area of MIL-101-NH₂ was $2154 \text{ m}^2 \text{ g}^{-1}$. The BET surface area of Pd@MIL-101-NH₂ was reduced to $1973 \text{ m}^2 \text{ g}^{-1}$, mainly due to the fact that Pd NPs occupy the pores of MIL-101-NH₂, which was close to the previous report [45].

Next we discuss the plausible mechanism of one-pot Suzuki-Knoevenagel reaction. The plausible mechanism of Pd@MIL-101-NH₂ in Suzuki reaction was depicted in Scheme 1. The catalytic cycle of the Suzuki coupling reaction is generally considered to be an oxidationaddition reaction of Pd(0) with a aryl halide aromatic hydrocarbon to form a complex of Pd(II), followed by metal transfer reaction with activated boric acid to form another complex of Pd(II). The complex is finally subjected to reduction-elimination to form a product and Pd(0) [46]. Scheme 2 is the illustration of the possible catalytic mechanism of Pd@MIL-101-NH2 in Knoevenagel condensation of benzaldehyde and malononitrile. In the first step, protons are taken from malononitrile by a Lewis basic site of the catalyst to form a carbon anion. In the second step, the carbon anion attacks the carbonyl carbon atom of benzaldehyde in the solution and forms a C-C bond by transferring a negative charge to the oxygen atom. In the third step, the oxyanion acquires protons from the Lewis basic site, forming water molecules. At the same time, the Lewis basic site of the catalyst is regenerated [47].

To characterize possible catalytic behavior of $Pd@MIL-101-NH_2$, a series of one-pot Suzuki-Knoevenagel reactions were carried out in different solvents and catalysts. Corresponding product yields were obtained by GC. Firstly, we tested several different solvents for the reaction catalyzed by $Pd@MIL-101-NH_2$. When the first step solvents



Fig. 2. TEM image of Pd@MIL-101-NH₂ (a) and corresponding size distribution of Pd nanoparticles (b). The inset in (a)is the EDX pattern.



Scheme 1. A plausible mechanism for the Suzuki condensation catalyzed by $Pd@MIL-101-NH_2$.

were ethanol and methanol, excellent yields (99.9% and 98.1%, respectively) were acquired (Table 1, Entries 1, 2). When solvents were replaced by DMF and toluene, poor yields were obtained (Table 1, Entries 3, 4). From these results, it can be seen that ethanol was the most optimum solvent for the one-pot reaction. Because the boiling point of ethanol is 78.4 °C, we researched effects of 60 °C and 70 °C for the reaction. In entry 5, we found that the reaction time was prolonged at 60 °C, so 70 °C is the best temperature. Next we verified that the bifunctional catalysts Pd@MIL-101-NH2 were essential for the one-pot reactions. In the first stage, we demonstrated that Pd NPs are critical to Suzuki reaction part of the one-pot reaction. We used MIL-101-NH2 and Pd@MIL-101-NH₂ catalysts to catalyze the one-pot reaction (Table 1, Entries 1, 7). In entry 7, we could find that no reaction occurred without the Pd NPs. Entry 6 and entry 8 also demonstrated the necessity of Pd NPs. In the second stage, it was proved that -NH2 group was indispensable to Knoevenagel reaction part of one-pot reaction. The one-pot reaction was catalyzed by Pd@MIL-101 and Pd@MIL-101-NH₂. It was found that the first-step, Suzuki reaction parts, were completed totally, but the catalysis of entry 6 could hardly catalyze the secondstep, Knoevenagel reaction parts, due to absence of -NH₂ group. Pd/C catalyst with poor repeatability could also catalyze the first-step reaction, but could not catalyze the second-step reaction due to the same reason (Table 1, Entry 9). Entry 10 showed that the one-pot reaction did not occur without any catalyst. Following this, a number of substituted



Scheme 2. A plausible mechanism for the Knoevenagel condensation catalyzed by Pd@MIL-101-NH₂.

Table 1

The one-pot Suzuki-Knoevenagel reaction of different substrates in different solvents using different catalysts.

	$R \xrightarrow{O} B(OH)_2 + 1 \xrightarrow{O} Catalyst} R \xrightarrow{O} Catalyst} R \xrightarrow{O} Catalyst} R \xrightarrow{O} Con$						
Entry	R	Catalyst	Solvent	Time (h)		Yield (%)	
				Step1	Step2	3	4
1^a	Н	Pd@MIL-101-NH ₂	Ethanol	1	2.5	99.9	99.9
2^a	Н	Pd@MIL-101-NH ₂	Methanol	4	2.5	98.1	53.7
3^a	Н	Pd@MIL-101-NH ₂	DMF	4	2.5	84.5	42.4
4^a	Н	Pd@MIL-101-NH ₂	Toluene	4	2.5	63.1	38.2
5^b	Н	Pd@MIL-101-NH ₂	Ethanol	1.6	3.2	99.9	99.9
6 ^c	Н	Pd@MIL-101	Ethanol	1	2.5	99.9	-
7^d	Н	MIL-101-NH ₂	Ethanol	4	2.5	-	-
8^e	Н	MIL-101	Ethanol	4	2.5	-	-
9 ^f	Н	Pd/C	Ethanol	4	2.5	99.9	-
$10^{ m g}$	Н	-	Ethanol	4	2.5	-	-
11^a	4-NO ₂	Pd@MIL-101-NH ₂	Ethanol	4	2.5	30.9	13.1
12^a	4-CH ₃ O	Pd@MIL-101-NH ₂	Ethanol	1	0.5	99.9	99.9
13^a	4-Cl	Pd@MIL-101-NH ₂	Ethanol	1	2.5	81.7	6.5
14^a	3-CH ₃ O	Pd@MIL-101-NH ₂	Ethanol	4	1	99.9	99.9

Reation conditions: 4-iodobenzaldehyde (1 mmol), phenylboronic acids (1.5 mmol), solvent (5 mL), K₂CO₃ (0.7 mmol), N₂ (0.1 MPa), 70 °C. ^b60 °C, other conditions are the same as a. Catalyst: 450 mg Pd@MIL-101-NH2 (Pd, 1 mmol%) was used. 50 mg Pd@MIL-101 (Pd, 1 mmol%) was used. 450 mg MIL-101-NH2 was used. 50 mg Pd@MIL-101-NH2 was used. 50 mg Pd@M MIL-101 was used. ^f0.4 mol% commercial 5% Pd/C was used. ^gNo catalyst was used.



Fig. 3. The recyclability studies performed for Pd@MIL-101-NH₂.

phenylboronic acid reactants were used to investigate the effect on the yield (Table 1, Entries 1, 11-14). The results illustrated that phenylboronic acids with electron withdrawing groups such as nitro (-NO₂) (Table 1, Entry 11) and chlorine (-Cl) (Table 1, Entry 13) had low yields, while the electron donating group (-OCH₃) had moderate to high vields (Table 1, Entries 12, 14).

Furthermore, it is obviously important to separate and reuse the catalyst. After the catalytic reaction, Pd@MIL-101-NH₂ can be recollected and reused easily. As illustrated in Fig. 3, the catalytic capability of Pd@MIL-101-NH₂ hardly declines after five catalytic cycles. Recycle XRD patterns of Pd@MIL-101-NH2 indicated the structure can be retained after catalytic reaction (Fig. 1). Recycle TEM images of Pd@ MIL-101-NH₂ further demonstrated the stability of the catalyst (Fig. S4). Therefore, the integrity of the framework was confirmed.

In summary, we have developed a bifunctional heterogeneous onepot catalyst for Suzuki-Knoevenagel reaction, Pd@MIL-101-NH₂, with Palladium nanoparticles and $-NH_2$ groups in its structure. It can be used as solid catalyst for Suzuki-Knoevenagel reaction with different substrates. It is easy to separate the catalyst from reaction mixture after catalytic reaction by simple centrifugation. The catalyst could be reused several times, and activity hardly declines. Further work is how to explore new one-pot catalytic reactions with Pd@MIL-101-NH2 and optimize the performance of Pd@MIL-101-NH₂.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.inoche.2019.02.042.

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