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Chemical vapor deposition of $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)$ for the synthesis of reusable Pd@ZIF-8 catalysts for the Suzuki coupling reaction

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ABSTRACT

A zeolite-imidazolium-framework-supported Pd-based heterogeneous catalyst (Pd@ZIF-8) was prepared by a metal-organic chemical vapor deposition method under mild conditions using $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)$ as the Pd precursor. N_2 adsorption and pore size distribution data showed that ZIF-8 and Pd@ZIF-8 both possessed high surface areas. Transmission electron microscopy images showed that Pd nanoparticles with sizes of about 1.5–3.5 nm were homogeneously dispersed on the ZIF-8 support in Pd@ZIF-8 . The Pd@ZIF-8 catalyst showed good activity in Suzuki coupling reactions with several different kinds of aryl halides. It could be reused at least six times without dramatic loss of activity or decomposition of the ZIF-8 structure.

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1. Introduction

Permanently microporous metal-organic framework (MOF) materials have attracted considerable attention for their large internal surface areas, uniform channels, nanometer-sized cavities, thermal stability, and chemical tailorability [1]. Zeolite imidazolate frameworks (ZIFs) are a very promising family of MOFs that have extended 3D crystalline structures constructed from tetrahedral metal ions (e.g., Zn, Co, In) bridged by imidazolate (Im) units. They combine the advantages of MOFs with higher stability and framework diversity. To date, a large variety of ZIFs with rich structural and topological diversity have been made by virtue of the flexibility with which the metals and links can varied [2,3]. In ZIF family, ZIF-8 ($[\text{Zn}(\text{Melm})_2]$, Melm = 2-methylimidazolate) has been widely studied due to its tunable pore size, chemical stability and thermal robustness, which make it a promising candidate for gas storage [4], molecular

separation [5], catalysis [6,7] and so on.

The Suzuki coupling reaction is one of the most effective ways to synthesize a C–C bond and is often catalyzed by homogeneous Pd catalysts, which usually provide high reaction rates and yields [8]. However, homogeneous catalysts have various drawbacks, especially the problem of recycling the catalyst, which leads to the loss of expensive metal and ligands, and to impurities in the products that must be removed [9,10]. To solve these problems, a heterogeneous Pd catalyst is an alternative option. Various solid supports, such as activated carbon [11,12], zeolites and molecular sieves [13–16], metal oxides [17–19], porous glass [20], ion exchange resin [21] and MOFs [22–25] have been used to stabilize the Pd nanoparticles in the coupling reaction.

In this work, ZIF-8 was employed as a support for Pd-supported catalysts prepared by the metal-organic chemical vapor deposition (MOCVD) method. The resulting Pd@ZIF-8 showed

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good activity for Suzuki coupling reactions without exclusion of air. The Pd@ZIF-8 catalyst can be used at least six times without obvious decrease in its activity. The powder X-ray diffraction (PXRD), Fourier-transform infrared (FT-IR) spectroscopy and N₂ adsorption results showed that the Pd@ZIF-8 remained intact, and the filtration test showed that no leaching of Pd occurred during the reaction process.

2. Experimental

2.1. Preparation of Pd@ZIF-8

The metal-organic compound Pd(C₃H₅)(C₅H₅) was synthesized according to literature reports [26,27]. ZIF-8 samples were synthesized via the solvothermal method described by Uyen et al. [7] with some modifications. Zn(NO₃)₂·6H₂O (1.88 g, 6.33 mmol) and 2-methylimidazole (H-Melm) (0.43 g, 5.82 mmol) were dissolved in dimethylformamide (DMF, 130 mL) and the solution was distributed into three glass vials that were placed in Teflon-lined autoclaves. The autoclaves were heated from 25 to 140 °C at a rate of 5 °C/min and maintained at 140 °C for 48 h, after which the yellow crystalline products were collected. The products were extracted with chloroform and the upper samples were washed with DMF and immersed in dichloromethane for 3 d. The ZIF-8 samples were vacuum-dried at 160 °C for 6 h before the Pd-loading process. Freshly activated ZIF-8 (500 mg) and Pd(C₃H₅)(C₅H₅) (25 mg) were placed in two separate vials in a Schlenk bottle and the system was evacuated to 1 Pa. The loading was carried out under static vacuum at 30 °C for 24 h. The hydrogenation procedure was carried out under 10⁵ Pa of H₂ at 23 °C for 1 h, after which the system was evacuated for 10 min to eliminate the hydrocarbon molecules generated from the decomposition of Pd(C₃H₅)(C₅H₅).

2.2. Suzuki cross-coupling reaction

The general procedure for the Pd@ZIF-8-catalyzed Suzuki coupling reaction was as follows. A 25-mL flask was charged with Pd@ZIF-8 (50 mg) and K₂CO₃ (0.276 g). The solvent (5 mL) and phenylboronic acid (1.1 mmol) were added followed

by the aryl halide (1.1 mmol). The mixture was maintained at 70 °C under aerobic conditions and stirred for the appropriate time. The reaction products were analyzed by GC-MS.

2.3. Characterization

PXRD analysis was recorded on a Rigaku D/Max-RB diffractometer using a Cu K_α monochromatized radiation source (λ = 0.15418 nm) operated at 40 kV and 100 mA. Surface functionalization was monitored by FT-IR spectroscopy using a Nicolet Impact 410 spectrometer with a resolution of 4 cm⁻¹. The Pd content was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2000 DV). Transmission electron microscopy (TEM) was carried out using a Philips CM200 FEG electron microscope (accelerating voltage 200 kV) to confirm the dispersion and size distribution of the Pd nanoparticles. The surface area, pore volume, and pore size distribution of the ZIF-8 support and the Pd@ZIF-8 catalysts were determined from N₂ adsorption-desorption isotherms at -196 °C using a Quantachrome Autosorb-IQ apparatus. X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALAB250 Surface Science instrument. A monochromatic Al K_α (1486.6 eV) X-ray source was used as the incident radiation. The binding energies were calibrated using the C 1s peak at 284.5 eV as a reference. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gaussian/Lorentzian peak shape.

3. Results and discussion

3.1. Preparation of catalysts

Over the past decade, there have been a number of reports on the immobilization of noble metal nanoparticles (e.g. Pd, Au, Ru and Pt) on MOFs by employing various preparation methods, such as impregnation [28,29], colloidal deposition [30], solid grinding [31]. In comparison, the MOCVD method can often be carried out under much milder conditions. This is a better choice for the relatively unstable MOF materials, and often provides smaller nanoparticles [22,32].

Fig. 1. PXRD patterns (a) and FT-IR spectra (b) of ZIF-8 and Pd@ZIF-8 before and after Suzuki coupling reactions.

In the present work, a highly volatile metal-organic compound, $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)$, was chosen as the palladium precursor. The precursor has a very high saturated vapor pressure at 30 °C and 1 Pa, the conditions under which the MOCVD process was carried out. The realistic Pd loading was 0.27 wt% as confirmed by ICP-AES.

The PXRD and FT-IR patterns of ZIF-8 and Pd@ZIF-8 are shown in Fig. 1. The characteristic signals of ZIF-8 were detected both before and after the loading and hydrogenation processes (Fig. 1(a)). The sharp pattern at $2\theta = 7.2^\circ$ in the PXRD pattern of ZIF-8 indicates that the crystallinity of ZIF-8 is relatively high. Similarly, no obvious change is observed and no characteristic absorption of the Pd precursor can be detected in the FT-IR spectra (Fig. 1(b)) after Pd loading, which indicates the complete decomposition of the Pd precursor in the hydrogenolysis process.

The N_2 adsorption-desorption isotherms of ZIF-8 and Pd@ZIF-8 are shown in Fig. 2(a). Type I isotherms according to the IUPAC classification are observed, which are typical for microporous materials. ZIF-8 exhibits a BET surface area of 1172 m^2/g , which is almost the same (1198 m^2/g) after Pd loading. Loading of Pd has almost no influence on the pore size distribution (Fig. 2(b)). These results prove that ZIF-8 is robust enough to maintain its crystal and pore structure during the

Pd-loading process. The mild conditions provided by the MOCVD method are clearly also important for the intactness of the ZIF-8 support after Pd loading.

The valence state change of Pd can be seen in the XPS spectra of $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)\text{@ZIF-8}$ and Pd@ZIF-8 (Fig. 3). The two main peaks related to $\text{Pd } 3d_{5/2}$ and $\text{Pd } 3d_{3/2}$, which are centered at XPS binding energies of 340.2 and 335.0 eV, respectively, and agree well with the values for Pd^{2+} , appear in the XPS spectrum of $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)\text{@ZIF-8}$ (Fig. 3(a)). The XPS peaks clearly change after the reduction process (Fig. 3(b)). The two new peaks related to $\text{Pd } 3d_{5/2}$ and $\text{Pd } 3d_{3/2}$ can both be deconvoluted into two peaks, which indicates the existence of two different Pd species in Pd@ZIF-8 . According to the NIST XPS Database, binding energies at 338.7 ($3d_{3/2}$) and 333.4 eV ($3d_{5/2}$) are characteristic of $\text{Pd}(0)$, whereas signals at 340.2 ($3d_{3/2}$) and 335.0 eV ($3d_{5/2}$) are characteristic of Pd^{2+} . These results reveal that $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)$ can be successfully reduced to $\text{Pd}(0)$ with hydrogen at room temperature, although some of the Pd metal on the surface of the catalyst remains oxidized because of exposure to air.

The size and dispersion of the Pd particles were obtained from TEM images (Fig. 4). The size distribution shows that most of the Pd particles have a size of 1.5–3.0 nm. However, some bigger particles (about 10 nm) that are caused by aggre-

Fig. 2. N_2 adsorption-desorption isotherms (a) and pore distribution (b) of ZIF-8 and Pd@ZIF-8 before and after Suzuki coupling reactions.

Fig. 3. XPS spectra of $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)\text{@ZIF-8}$ (a) and Pd@ZIF-8 before (b) and after (c) Suzuki coupling reactions.

Fig. 4. TEM images (a, b, c) and particle size distribution (d) of Pd@ZIF-8 catalytic material.

gation are also observed. ZIF-8 exhibits a sodalite-like structure with a pore size of 1.2 nm and a relatively small pore window of 0.35 nm. Esken et al. [32] described three possibilities for the deposition of nanoparticles on MOFs. In the first case, the particles are typically larger than the cavity size and have a preferred anchoring close to the outer surface of the MOF. In the second case, the particles are evenly distributed throughout the volume of the MOF crystal but still exhibit a broad size distribution, with the average particle size exceeding the dimensions of the pores. In the third case, particles with a narrow size distribution matching the dimensions of the cavities are homogeneously distributed over the volume of the MOF. In the current work, the average size of the Pd particles is a little larger than the ZIF-8 cavity size, and we thus expect that the majority of particles can be classified into the second case. At the same time, the much larger particles may be expected to anchor close to the outer surface of ZIF-8.

3.2. Suzuki coupling reaction

We first tested the catalytic activity of Pd@ZIF-8 in a Suzuki-Miyaura reaction between bromobenzene and phenylboronic acid, and the results are summarized in Table 1. The reactions were carried out in a batch reactor at 70 °C without exclusion of air. Previously studies have showed that solvents and bases had remarkable influences on the reactivity of the Suzuki reaction. We are interested in using green and cheaper catalysts in these reactions to replace catalysts that have expensive phosphine ligands. Although in water, the catalyst system afforded the corresponding coupling product in moderate yield, acetone, DMF, and THF were proven to be poor solvents for the same process. High activity was reproducibly found in MeOH. Acceptable conversion was also found in EtOH, but a mixture of DMF/H₂O in a 1:1 ratio was not suitable for the pre-

Table 1

Effect of solvent and base on the Suzuki-Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid using Pd@ZIF-8 as a catalyst.

Solvent	Base	T (°C)	Time (h)	Yield (%)
THF	K ₂ CO ₃	70	5	11.6
DMF	K ₂ CO ₃	70	5	12.4
Acetone	K ₂ CO ₃	70	5	5.8
EtOH	K ₂ CO ₃	70	5	76.8
MeOH	K ₂ CO ₃	70	5	83
H ₂ O	K ₂ CO ₃	70	5	45.8
DMF:H ₂ O = 1:1	K ₂ CO ₃	70	5	15.5
MeOH	Na ₂ CO ₃	70	5	80.4
MeOH	Et ₃ N	70	5	23.8
MeOH	KOH	70	5	85.6
MeOH	Na ₃ PO ₄	70	5	84.6

sent system. Under the same conditions, various bases such as Na₂CO₃, K₂CO₃, KOH, Et₃N, and Na₃PO₄ were examined for the reaction. The results revealed that the inorganic bases were more effective than organic base of Et₃N and hence the economically cheaper K₂CO₃ was chosen as the base for these coupling reactions.

With the optimized solvent and base in hand, we investigated the activity of Pd@ZIF-8 for various substrates. The results are summarized in Table 2. In general, all the reactions

Table 2

Suzuki-Miyaura cross-coupling of aryl halides and phenylboronic acid catalyzed by Pd@ZIF-8 catalysts.

<div><div><div><div><div><div></div><div>X</div></div></div><div><div></div><div>R</div></div></div><div>+</div><div><div><div><div><div></div><div>B(OH)₂</div></div></div><div><div></div><div></div></div></div><div><div><div><div><div><div></div><div>Pd@ZIF-8</div></div><div><div>MeOH, K₂CO₃</div><div>70 °C</div></div></div></div><div><div></div><div></div></div></div><div><div><div><div><div></div><div></div></div><div><div></div><div>R</div></div></div></div></div></div></div></div></div>					
Aryl Halide	Product	Time (h)	T (°C)	Yield (%)	TOF (h ⁻¹)
<div><div><div></div><div>I</div></div></div>	<div><div><div><div></div><div></div></div></div></div>	1	70	>99	2486
<div><div><div></div><div>Br</div></div></div>	<div><div><div><div></div><div></div></div></div></div>	5	70	83	411
<div><div><div><div></div><div>H₃C</div></div><div><div></div><div>Br</div></div></div></div>	<div><div><div><div></div><div></div></div><div><div></div><div>H₃C</div></div></div></div>	5	70	82	408
<div><div><div><div></div><div>CH₃</div></div><div><div></div><div>Br</div></div></div></div>	<div><div><div><div></div><div>CH₃</div></div><div><div></div><div></div></div></div><div><div></div><div></div></div></div>	5	70	81	403
<div><div><div><div></div><div>Br</div></div><div><div></div><div>OCH₃</div></div></div></div>	<div><div><div><div></div><div></div></div><div><div></div><div>OCH₃</div></div></div></div>	5	70	79	393
<div><div><div><div></div><div>Br</div></div><div><div></div><div>COCH₃</div></div></div></div>	<div><div><div><div></div><div></div></div><div><div></div><div>COCH₃</div></div></div></div>	1	70	>99	2486
<div><div><div><div></div><div>H₃C</div></div><div><div></div><div>Cl</div></div></div></div>	<div><div><div><div></div><div></div></div><div><div></div><div>H₃C</div></div></div></div>	10	70	15	95
<div><div><div></div><div>Cl</div></div></div>	<div><div><div><div></div><div></div></div></div></div>	10	70	18	114

were very clean and no self-coupling of phenylboronic acid could be detected. As expected, the aryl iodide was rapidly converted to the corresponding biaryl product in excellent yields. This coupling reaction was equally effective with both electron-rich and electron-poor aromatic bromoarene derivatives, and the reactions proceeded smoothly to furnish the Suzuki product in good to excellent yields in relatively short reaction times. The less reactive chlorobenzene and *para*-chlorotoluene showed only a relatively low conversion even with longer reaction times.

3.3. Recyclability

Recovery and reuse of the catalyst and leaching of Pd metal into the solution are important issues in coupling reactions, especially when the reactions are carried out under heterogeneous conditions. MOF-5, the most common MOF material, has been applied in a lot of reactions, such as hydrogenation [33–35], oxidation [36], and Suzuki coupling reactions [22]. NPs@MOF-5 catalysts often show an acceptable activity in the first run; however, because of their water sensitivity, the activity decreases sharply when the catalysts are reused. ZIF-8 combines the advantages of MOF-5 (large internal surface area, uniform channel, nanometer-sized cavities) with a higher chemical stability, which gives us good reason to believe that Pd@ZIF-8 would have a better stability. The reusability-testing results from the reaction of iodobenzene and phenylboronic acid are shown in Fig. 5. The catalyst was simply washed with methanol without any other activating treatments before every reaction cycle. The conversion of iodobenzene is slightly decreased after every reaction cycle for the residual reactants as determined by FT-IR data. However, if the reaction time is increased to 2 h, iodobenzene can still be completely converted in each run of the reaction. The TEM images (Fig. 6) show that no growth or aggregation of the catalyst happened during the reaction process.

After demonstrating the reusability of Pd@ZIF-8, the stability of the catalyst was confirmed by performing PXRD, FT-IR, N₂ adsorption, and XPS characterization on the used Pd@ZIF-8 catalyst. It can be seen (Fig. 1(a)) that the crystal structure of ZIF-8 is intact after the Suzuki coupling reaction. Again, no signals of Pd were detected, which means that no apparent aggregation happened during the reaction process. The strong

Fig. 5. Recyclability of the Pd@ZIF-8 catalyst.

intensity peak at $2\theta = 7.2^\circ$ proves that the high crystallinity of the catalyst was preserved after the reactions. However, some differences can be detected in the FT-IR (Fig. 1(b)) and pore size distribution results (Fig. 2(b)). New absorptions at 835, 855, 1376, and 1486 cm^{-1} , which correspond to the vibration of C–H in the aromatic ring appeared in the FT-IR spectrum. This indicates that some of the residual reactants are left in the catalyst. For the same reason, the number of pores with dimensions of around 0.8–1.0 nm decreased and the number of wider pores (around 1.2–1.4 nm) increased. Another possible reason for these changes is that the short-range arrangement of the ZIF-8 crystal structure was partly damaged, but that this could not be detected by PXRD, FT-IR, or N₂ adsorption experiments. The XPS pattern of the used catalyst is shown in Fig. 3. The two Pd species can still be seen, and additional oxidation of Pd does not appear to occur, indicating that the Pd is stable during the Suzuki coupling reaction. In conclusion, the Pd@ZIF-8 catalyst has great stability owing to the thermal and chemical rigidity of the ZIF-8 support. The catalyst is easily recycled and can be reused at least six times in Suzuki coupling reactions.

3.4. Filtration test

The presence of leached Pd species in solution was examined by a filtration test for the coupling reaction of iodobenzene and phenylboronic acid. After about 24% completion (5 min

Fig. 6. TEM images (a, b) and particle size distribution (c) of Pd@ZIF-8 after reaction.

Fig. 7. Filtration test results for Pd@ZIF-8.

reaction time), the solution was filtered off and the filtrate was stirred at 70 °C with further addition of K_2CO_3 (0.276 g). Progress of the reaction was monitored by GC-MS. The results (Fig. 7) showed that further conversion was not possible after the catalyst was filtered out. Thus, no active Pd species leached into the solution during the reaction, and this agrees well with the ICP results.

4. Conclusions

The embedding of Pd nanoparticles into ZIF-8 has been successfully carried out with the MOCVD method. The resulting Pd@ZIF-8 has a very high BET surface area, and TEM images showed that Pd particles with sizes of 1.5–3.5 nm were well dispersed on the ZIF-8 support. Pd@ZIF-8 was used as a heterogeneous catalyst for Suzuki coupling reactions and achieved good activity in methanol under an open atmosphere with several different aryl halides. The Pd@ZIF-8 catalyst was simply recycled for the next run without extra treatment and could be used at least six times without dramatic reduction in its activity. PXRD, FT-IR, and N_2 adsorption experiments proved the intactness of the catalyst after several runs of the reaction, and this stability is believed to be a result of the chemical robustness of ZIF-8.

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Graphical Abstract

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Chemical vapor deposition of $Pd(C_3H_5)(C_5H_5)$ for the synthesis of reusable Pd@ZIF-8 catalysts for the Suzuki coupling reaction

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Pd@ZIF-8 was prepared by the metal-organic chemical vapor deposition method using $Pd(C_3H_5)(C_5H_5)$ as the Pd precursor. The Pd@ZIF-8 catalyst, which contains well-dispersed Pd particles, was an effective and recyclable catalyst in Suzuki coupling reactions.

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MOCVD法制备Pd@ZIF-8催化剂及其催化Suzuki反应性能

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摘要: 以金属有机骨架化合物ZIF-8为载体, Pd(C₃H₅)(C₅H₅)为金属有机前体, 采用金属有机气相沉积方法在室温下制备了Pd@ZIF-8催化剂. Pd纳米粒子在ZIF-8载体上均匀分布, 粒子尺寸约为1.5–3.5 nm. Pd@ZIF-8在温和条件下对多种卤代芳烃和苯硼酸的偶联反应均具有良好的活性. ZIF-8优异的化学稳定性不仅保证了其在制备过程中结构的完整, 而且赋予了催化剂优异的循环使用性能. 反应后Pd@ZIF-8材料的晶体结构、孔结构以及粒子分布均未发生明显的变化.

关键词: 钯; ZIF-8; 金属有机气相沉积; Suzuki偶联反应

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