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Ni@Pd core-shell nanoparticles supported on a metal-organic framework as highly efficient catalysts for nitroarenes reduction

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1. Introduction

Palladium (Pd) is well-known as an important noble metal catalyst and is widely used in hydrogenation, oxidation, coupling, and other reactions [1–4]. Heterogeneous catalysis by Pd is typically based on supported Pd nanoparticles (NPs). However, the catalytic reactions associated with these materials occur solely on the NP surfaces, such that the majority of the metal atoms, in the NP cores, are wasted [5]. It is therefore beneficial to expose as many Pd atoms as possible so as to achieve high specific activity and reduce the usage of this precious metal. In recent years, core-shell NPs have attracted intense interest as a result of their superior performance com-

ABSTRACT

Ni@Pd core-shell nanoparticles with a mean particle size of 8–9 nm were prepared by solvothermal reduction of bivalent nickel and palladium in oleylamine and trioctylphosphine. Subsequently, the first-ever deposition of Ni@Pd core-shell nanoparticles having different compositions on a metal-organic framework (MIL-101) was accomplished by wet impregnation in *n*-hexane. The Ni@Pd/MIL-101 materials were characterized by powder X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, and energy-dispersive X-ray spectroscopy and also investigated as catalysts for the hydrogenation of nitrobenzene under mild reaction conditions. At 30 °C and 0.1 MPa of H₂ pressure, the Ni@Pd/MIL-101 gives a TOF as high as 375 h⁻¹ for the hydrogenation of nitrobenzene and is applicable to a wide range of substituted nitroarenes. The exceptional performance of this catalyst is believed to result from the significant Ni-Pd interaction in the core-shell structure, together with promotion of the conversions of aromatics by uncoordinated Lewis acidic Cr sites on the MIL-101 support.

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pared with monometallic noble metal NPs, an effect that arises due to core-shell interactions [6–10]. Although core-shell bimetallic NPs synthesized with two noble metals show excellent catalytic activity, the synthesis of such NPs by combining an inexpensive metal core with a noble metal shell is more attractive [11].

Ni@Pd bimetallic NPs have been studied intensely because both Ni and Pd are group VIII metals and thus have similar peripheral electron configurations. Moreover, they both are active in the hydrogenation of unsaturated compounds [12,13]. Hyeon and co-workers [11] successfully synthesized Ni@Pd core-shell NPs through thermal decomposition of palladium and nickel precursors, although the recovery of these NPs from

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the reaction mixture was difficult. Sun's group [14] prepared the same Ni@Pd NPs by a one-step method, and these NPs, supported on graphene, exhibited high catalytic activity during Suzuki-Miyaura cross-coupling reactions.

Functionalized anilines are important intermediates in the pharmaceutical, chemical, agrochemical, and dye industries [15]. The traditional non-catalytic reduction of nitroarenes using stoichiometric reducing reagents such as sodium borohydride, silanes, and hydrazine derivatives often causes serious environmental problems [16], and so catalytic hydrogenation with supported metal catalysts has captured widespread research interest in recent years [17,18]. Under mild reaction conditions, heterogeneous noble catalysts such as Au/TiO₂, Au/ γ -Al₂O₃, and Pd-Pt-carbon nanotubes (CNTs) have exhibited highly selective reduction of nitroarenes. However, the majority of these transformations were associated with relatively low turnover frequency (TOF) values that would need to be further improved to realize the practical applications of noble-metal catalysts [19–21].

In the present work, Ni@Pd core-shell NPs with different Ni/Pd molar ratios were synthesized using a sequential reduction method. In this process, Ni and Pd precursors were sequentially reduced by oleylamine (OAm) and trioctylphosphine (TOP) to produce the desired NPs. Subsequently, these NPs were deposited on a MIL-101 metal-organic framework (MOF) using a simple impregnation method. The novel MIL-101 supported Ni@Pd NPs that resulted were found to be highly efficient in the reduction of nitroarenes under mild reaction conditions. Cr(III)-based MIL-101, a mesoporous MOF with the molecular formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$ (n = 25) was chosen because it has a high surface area, good stability, and numerous potentially active Cr sites (up to 3.0 mmol/g) upon removal of the terminal water molecules [22]. The Lewis acidity of MIL-101 has been demonstrated to play a significant role in promoting the reactivity of aromatic substrates [2,23]. In addition, we have previously shown that Pd NPs can be well dispersed on this MOF and subsequently show high activity and stability [24].

2. Experimental

2.1. General

All chemicals were obtained from commercial sources and were used without any further purification. Powder X-ray diffraction (XRD) patterns of MIL-101 samples were obtained using a Rigaku diffractometer (D/MAX-IIIA, 3 kW) with Cu K_{α} radiation (40 kV, 30 mA, λ = 0.1543 nm). Brunauer-Emmett-Teller (BET) surface areas and pore volumes of the materials were assessed with a Micromeritics ASAP 2020 instrument based on N₂ adsorption at -196 °C after evacuation at 150 °C for 12 h. The Ni and Pd contents of the samples were quantitatively determined by atomic absorption spectroscopy (AAS) with a HITACHI Z-2300 instrument. Fourier transform infrared (FT-IR) spectra of the samples were obtained on a Thermo Scientific Nicolet iS10 spectrometer with a Smart OMNI accessory. transmission Transmission electron

microscopy (TEM) micrographs of the samples were acquired using a JEM-2010HR (JEOL).

2.2. Synthesis of Ni@Pd NPs

Palladium(II) bromide (PdBr2, 26.6 mg, 0.1 mmol), nickel(II) acetate tetrahydrate (Ni(ac)2·4H2O, 24.9 mg, 0.1 mmol), TOP (0.5 mL), and OAm (10.0 mL) were added to a 25 mL Teflon-lined, stainless steel autoclave contained in a glovebox filled with nitrogen at room temperature. This mixture was then heated at 255 °C for 2 h and subsequently allowed to cool slowly to room temperature. The NP product was separated from the reaction mixture by adding 40 mL isopropanol, followed by two centrifugations at 10000 rpm for 10 min. The NPs were further purified and collected by first dispersing them in anhydrous *n*-hexane (5 mL) then adding a 1:1 mixture of ethanol and isopropanol and centrifuging at 10000 rpm for 10 min. The resulting NP powder was redispersed in anhydrous n-hexane. The prepared Ni@Pd core-shell NPs had a Ni:Pd molar ratio of approximately 1:1. Under the same conditions, the use of 0.1 mmol PdBr2 with 0.5 or 0.05 mmol Ni(ac)2·4H2O gave Ni@Pd core-shell NPs with Ni:Pd molar ratios of 5:1 and 0.5:1, respectively. Monometallic Ni and Pd NPs were synthesized using the same method.

2.3. Synthesis of Ni@Pd/MIL-101 and other catalysts

Ni@Pd/MIL-101 catalysts were synthesized using an impregnation method. Typically, 400 mg of activated MIL-101 was dispersed in 10 mL of anhydrous *n*-hexane and stirred for 1 h at room temperature. The previously-prepared dispersion of NPs in *n*-hexane was then added dropwise to the above solution followed by stirring for 12 h. Each impregnated MIL-101 sample was washed with anhydrous *n*-hexane until colorless filtrate was obtained and then slowly dried under vacuum at 150 °C for 12 h to obtain Ni@Pd/MIL-101. Samples of Ni/MIL-101, Pd/MIL-101, and Ni@Pd/AC were synthesized using the same method, while NiPd/MIL-101 and Ni@Pd/En-MIL-101 were synthesized following procedures previously reported in the literature [25]. The resulting Ni and Pd concentrations in the catalysts were determined by AAS.

2.4. Nitroarenes reduction reaction

The substrate (0.5 mmol), Ni@Pd/MIL-101 catalyst (0.023 g, Pd 0.2 mol%), and ethyl acetate (4 mL) were added to a Schlenk tube, and the mixture was vigorously stirred with an affixed hydrogenation balloon at room temperature. Following the reaction, the solid catalyst was removed from the solution by filtration and washed with ethyl acetate. The product yields were determined by gas chromatography-mass spectrometry (GC/MS, Shimadzu GCMS-QP5050A) with a 0.25 mm × 30 m DB-WAX capillary column. Parameters were as follows: initial oven temperature, 100 °C, 1 min; ramp, 20 °C/min; final temperature, 280 °C; final time, 5 min.

During recyclability trials, reactions were performed under the same conditions as above, except using recovered catalyst. Each time, the catalyst was separated from the reaction mixture at the end of the reaction, washed with ethyl acetate and then dried at 150 °C under vacuum prior to reuse.

3. Results and discussion

3.1. Characterization results of the materials

The XRD pattern of the as-synthesized MIL-101 is in good agreement with previously published XRD patterns (Fig. 1). There is no apparent loss of crystallinity and no identifiable peaks attributed to the metal NPs after impregnation, indicating that the MIL-101 framework maintained its structural integrity and that very small NPs were present on the MIL-101. Some minor changes in the relative peak intensities were observed in the case of the Ni@Pd/En-MIL-101, which could be related to grafting of ethane diamine onto the Cr sites of the framework.

The N₂ adsorption isotherms of the samples were subsequently acquired at -196 °C, as shown in Fig. 2, and the BET surface areas were calculated by choosing N₂ adsorption points in the p/p_0 range of 0.05–0.3. BET surface areas of 2912, 2790, 2685, 2635, 2449, and 2324 m²/g were determined, along with pore volumes of 1.5, 1.45, 1.39, 1.37, 1.36, and 1.33 cm³/g, for the as-synthesized MIL-101, Ni/MIL-101, Pd/MIL-101, 0.15%Ni@0.45%Pd/MIL-101, 0.26%Ni@0.46%Pd/MIL-101, and 1.51%Ni@0.46%Pd/MIL-101 (where the numerical values indicate mass percentages), respectively. The slight decreases in N₂ adsorption amounts and BET surface areas indicate that the core-shell NPs supported on the MIL-101 either occupied or blocked part of the pores or cavities of the MOF material.

Fig. 3 presents TEM images of the unsupported metal NPs and Ni@Pd/MIL-101 samples. As shown in Fig. 3(a)-(c), the average sizes of the unsupported NPs were all in the range of 8–9 nm. This result indicates that the Ni:Pd ratio does not significantly affect the NP size. In addition, Fig. 3(d)-(e) demonstrates that the metal NPs were well dispersed on MIL-101.



Fig. 1. Powder XRD patterns of (1) MIL-101 (as-synthesized), (2) 0.26%Ni@0.46%Pd/MIL-101, (3) 0.42%Pd/MIL-101, (4) 0.26%Ni/ MIL-101, (5) 0.26%Ni0.46%Pd/MIL-101, (6) reused 0.26%Ni@ 0.46%Pd/MIL-101, and (7) 0.26%Ni@0.46%Pd/En-MIL-101.



Fig. 2. N_2 adsorption-desorption isotherms of various materials at -196 °C. (1) MIL-101; (2) Ni/MIL-101; (3) Pd/MIL-101; (4) 0.15%Ni@ 0.45%Pd/MIL-101; (5) 0.26%Ni@0.46%Pd/MIL-101; (6) 1.51%Ni@ 0.46%Pd/MIL-101. Open symbols indicate desorption branches.

However, increasing the metal loading to approximately 2% (by mass) evidently generated metal NP aggregates (Fig. 3(f)). The core-shell NPs are also observed to have a polycrystalline structure. In agreement with the literature reports [14], the outer layer has a lattice fringe distance of 0.232 nm that may represent the (111) planes of face-centered cubic (fcc) Pd with a normative lattice spacing of approximately 0.223 nm. The interlayer in the core has a lattice spacing of 0.214 nm and represents a variation of the crystal lattice parameters of Ni(111). In contrast, the standard lattice spacing of Ni(111) is on the order of 0.203 nm [26]. The observed differences between the Pd(111) and Ni(111) lattice spacing and the standard values can be attributed to the interaction between the Ni and Pd in the NPs. EDS analysis determined that the Ni@Pd/MIL-101 was composed of C, O, Cr, P, Ni, and Pd (Fig. 3(i)). The Cu signal in the EDS data arises from the sample holder, while the P signal comes from the TOP used in the samples preparation process.

The FT-IR spectra of 0.26%Ni@0.46%Pd/MIL-101 and MIL-101 samples are shown in Fig. 4. The aliphatic C-H stretching vibrations (at 2800–3000 cm⁻¹) observed for Ni@Pd/MIL-101 indicate the presence of TOP, possibly coordinated to a Lewis acid center [2,27]. This observation suggests the probable grafting of P groups onto the coordinate-ly-unsaturated Cr sites in the MIL-101. In addition, the EDS results also show a P peak, confirming the presence of the phosphine ligand in the sample, whereas a N signal from the OAm is not present (Fig. 3(i)). The phosphine ligands may bridge between the NPs and the unsaturated Cr sites, allowing the NPs to be highly dispersed on the MIL-101.

3.2. Nitroarenes reduction catalyzed by Ni@Pd/MIL-101

The catalytic hydrogenation of nitrobenzene was performed at 30 °C under H_2 at a pressure of 0.1 MPa, and the results are summarized in Table 1. The original MIL-101 was found to exhibit no activity in this catalytic reaction system (Table 1,



Fig. 3. TEM images of unsupported Ni@Pd NPs having Ni:Pd molar ratios of 0.5:1 (a), 1:1 (b), and 5:1 (c); TEM images of 0.15%Ni@0.45%Pd/MIL-101 (d), 0.26%Ni@0.46%Pd/MIL-101 (e), 1.51%Ni@0.46%Pd/MIL-101 (f), and 0.26%Ni@0.46%Pd/MIL-101 following reuse over five trials (g); HRTEM image of Ni@Pd NPs (with Ni:Pd molar ratio of 1:1) (h); Energy dispersive X-ray (EDS) spectrum of the as-synthesized 0.26%Ni@0.46%Pd/MIL-101 (i).

entry 1). In addition, the activity of the catalysts were highly dependent on the Ni-Pd compositions. Evidently, the core-shell Ni@Pd/MIL-101 samples were capable of higher activity (Table 1, entries 2–4). The results of the nitrobenzene reductions show that the best performance was obtained from the 0.26%Ni@0.46%Pd/MIL-101 (Table 1, entry 3), with 71% conversion of nitrobenzene to aniline within 1 h at 30 °C. Using the 0.26%Ni@0.46%Pd/MIL-101 catalyst, a number of solvents were also screened, and this process indicated that ethylacetate is the best solvent for this transformation under the current conditions (Table 1, entry 5). In ethanol, the aniline product was observed to further react with the solvent to produce un-



Fig. 4. Infrared spectra of (1) Ni@Pd/MIL-101 and (2) MIL-101.

wanted side products such as *N*-ethylaniline, leading to a lower yield. The optimized Ni@Pd/MIL-101 catalyst gave a TOF value of 375 h⁻¹, a very high value under such mild conditions compared to results reported in the literature [20,28,29].

The catalytic activity of the 0.26%Ni@0.46%Pd/MIL-101 was almost twice that of the monometallic Pd catalyst (Table 1, entry 6), possibly because of the increased dispersion of Pd on

Table 1

Results from the hydrogenation of nitrobenzene with various catalysts.

	$NO_2 \xrightarrow{1 \text{ atm } H_2} 30 ^{\circ}\text{C}$	NH ₂		
Entry	Catalyst	Solvent	Yield ^a	TOF
			(%)	(h-1)
1	MIL-101	EtOH	0	0
2	1.51%Ni@0.46%Pd/MIL-101	EtOH	65	325
3	0.26%Ni@0.46%Pd/MIL-101	EtOH	71	355
4	0.15%Ni@0.45%Pd/MIL-101	EtOH	51	255
5	0.26%Ni@0.46%Pd/MIL-101	EtOAc	75	375
6	0.42%Pd/MIL-101	EtOAc	39	195
7 ^b	0.26%Ni/MIL-101	EtOAc	0	0
8	NiPd/MIL-101	EtOAc	41	205
9	0.26%Ni@0.46%Pd/En-MIL-101	EtOAc	23	115
10	0.26%Ni@0.47%Pd/AC	EtOAc	3	15

Reaction conditions: nitrobenzene (0.5 mmol), catalyst (0.023 g, Pd 0.2 mol%), solvent (4 mL), 30 °C, 1 h, H_2 (0.1 MPa). ^a Yields were determined by GC-MS analysis. ^b Catalyst (0.023 g), 12 h.

the Ni core, generating a greater quantity of exposed Pd active sites, as well as the Ni–Pd interaction resulting from the core-shell structure. The catalytic activity of this material was also significantly higher than that of the bimetallic alloy NiPd/MIL-101 catalyst (Table 1, entry 8). Notably, Ni is not active in this reaction system even with a much longer reaction time (Table 1, entry 7).

For comparison purposes, the amine-grafted material 0.26%Ni@0.46%Pd/MIL-101 was also tested in the reduction of nitrobenzene under the optimized reaction conditions. The use of this catalyst led to inferior activity in the reduction (Table 1, entry 9), giving only a 23% yield of aniline. The remarkably reduced activity of Ni@Pd/MIL-101 upon amine grafting on the unsaturated chromium sites of MIL-101 suggests that the uncoordinated Lewis acidic Cr sites play an important role in the nitrobenzene reduction. This result correlates well with the low activity observed for 0.26%Ni@0.47%Pd/AC, which also possesses low Lewis acidity (Table 1, entry 10). These findings

also agree with observations that activated MIL-101 can promote the conversions of aromatics through the interaction between the uncoordinated Lewis acidic Cr sites and the aromatic rings [22,30].

We attempted to extend this catalytic system to the reduction of a series of nitroarenes, using the optimized 0.26%Ni@0.46%Pd/MIL-101 catalyst, with the results summarized in Table 2. It can be seen that Ni@Pd/MIL-101 was highly active and selective for the reduction of most of the substrates, indicating the high versatility of the MOF-supported core-shell catalyst. Substituted nitroarenes containing electron-withdrawing or electro-donating functional groups all underwent excellent conversions with good selectivity to the corresponding anilines (Table 2, entries 1–6).

The chemoselective hydrogenation of nitroarenes having additional unsaturated substituents is a significant challenge. However, our Ni@Pd/MIL-101 catalyst was found to be highly active and chemoselective for the hydrogenation of various

Table 2

Hydrogenation of various substituted nitroarenes over the Ni@Pd/MIL-101 catalyst.

Entry	Substrate	Product	Time (h)	Con. (%)	Sel. (%)	TOF (h-1)	Entry	Substrate	Product	Time (h)	Con. (%)	Sel. (%)	TOF (h-1)
1	HO NO2	HO NH2	2	97	99	243	11	NO ₂	NH ₂	2.5	100	99	198
2	H ₂ N NO ₂	H ₂ N	2	100	99	248	12			1	100	99	495
3	NO ₂	NH ₂	1	100	99	495	13		NH ₂	5	98	88	96
4	HO NO ₂	HO NH2	1	100	99	495	14		O NH2	1	100	99	495
5	NO ₂	NH ₂	1	96	99	475	15			2	100	99	248
6	F NO ₂	F NH ₂	1	95	99	470	16 ª			18	51	99	14
7	O NO2	O NH2	1	100	99	495	17 ^a			18	72	99	20
8	NO ₂	NH2	1	95	99	470	18			18	100	92	26
9	O NO2	0, NH2	1	97	95	461	19 a	NO ₂	0 0 NH2	18	100	73	20
10	NO ₂ H ₂ N	O H ₂ N	1	100	99	495							

Reaction conditions: substrate (0.5 mmol), 0.26%Ni@0.46%Pd/MIL-101 (0.023 g, Pd 0.2 mol%), ethyl acetate (4 mL), 30 °C, 1 bar H₂. ^a Solvent: ethyl acetate and dichloromethane mixture (1:1, 4 mL).

substituted nitroarenes, with the exception of nitrostyrene (Table 2, entries 7-19). In addition, the ethenyl moiety is so active that both the nitro and ethenyl groups are simultaneously hydrogenated (Table 2, entry 11). In most cases, the selectivity for the functionalized aniline was >99%, with a nitroarene conversion of 100%. The exception was the hydrogenation of nitroarenes containing polyunsaturated substituents and unsaturated heterocyclic groups, for which lower activity were observed (Table 2, entries 16-19).

3.3. Recycling of the Ni@Pd/MIL-101 catalyst

The recyclability of the Ni@Pd/MIL-101 catalyst was examined during nitrobenzene reduction under the optimized conditions. The results presented in Fig. 5 indicate that only a small loss in conversion and selectivity resulted from the reduction of nitrobenzene over up to five replicate trials. After five reuses, the XRD pattern of the catalyst showed no appreciable change in the crystallinity of the MIL-101 material (Fig. 1). However, the Ni@Pd/MIL-101 catalyst did exhibit slight aggregation, which may have been responsible for the small decline in the catalytic performance (Fig. 3(g) and Fig. 5).

4. Conclusions

We have achieved the first-ever successful synthesis of Ni-Pd core-shell NPs by a sequential reduction method followed by deposition on an MOF support. The as-prepared Ni@Pd/MIL-101 catalysts are highly active and selective during the hydrogenation of nitroarenes to anilines. Under mild reaction conditions (30 $^{\circ}\text{C},~\text{H}_2$ pressure 0.1 MPa), the Ni@Pd/MIL-101 gives a TOF as high as 375 h⁻¹ for the hydrogenation of nitrobenzene and exhibits a broad substrate scope for substituted nitroarenes. The superior performance of the catalyst can be attributed to the strong Ni-Pd interaction in the core-shell structure, together with the role of the MIL-101 support in promoting the conversions of aromatics through uncoordinated Lewis acidic Cr sites. The strategy and approach disclosed here are general and could be extended to the design and development of other novel bimetal NP catalysts.



Fig. 5. Reuse of Ni@Pd/MIL-101.

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