

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: <http://www.tandfonline.com/loi/lcyc20>

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To cite this article: Xia Chen, Xiao-Yu Zhou, Hong Wu, Yi-Zhu Lei, & Jin-Hui Li (2018): Highly efficient reduction of nitro compounds: Recyclable Pd/C-catalyzed transfer hydrogenation with ammonium formate or hydrazine hydrate as hydrogen source, Synthetic Communications, DOI: [10.1080/00397911.2018.1484924](https://doi.org/10.1080/00397911.2018.1484924)

To link to this article: <https://doi.org/10.1080/00397911.2018.1484924>



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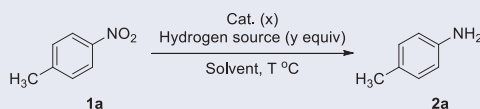
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ABSTRACT

Herein, we described a highly efficient heterogeneous Pd/C-catalyzed transfer hydrogenation of nitro compounds for the synthesis of primary amines, using ammonium formate and hydrazine hydrate as hydrogen source independently. The products were obtained with up to >99% yield. Furthermore, gram scale and recycling of catalyst had been tested with well results.

GRAPHICAL ABSTRACT



ARTICLE HISTORY

Received 4 February 2018


KEYWORDS

Ammonium formate; hydrazine hydrate; nitro compounds; palladium; transfer hydrogenation

Heterogeneous catalyst-catalyzed hydrogenation and/or transfer hydrogenation of compounds with C=C, C=O, C=C, N=N, or -NO₂ functional groups is one of the most direct and efficient approaches to obtain corresponding saturated compounds.^[1] A variety of metal catalysts and transfer hydrogenation systems had been successfully applied to this reaction over the last few decades. Among the various catalytic transfer hydrogenation systems,^[1a] so far, Rh,^[2] Ru,^[3] Ir,^[4] Cu,^[5] Fe,^[6] Co,^[7] Au,^[8] Pd,^[9] boron,^[10] and organocatalyst^[11] have been widely employed in transfer hydrogenations of unsaturated compounds. But the exploration of heterogeneous catalysis system^[1c-1e] and hydrogen source always are the topics for chemists.

Palladium catalysis system is always a popular choice for the reduction of unsaturated compounds by hydrogenation or transfer hydrogenation. Heck et al.^[12] reported palladium-catalyzed transfer hydrogenation of alkynes for the synthesis of corresponding alkenes in the presence of triethylamines and formic acid. Ranu et al.^[13] reported chemoselective hydrogenation of α , β -unsaturated sulfones and phosphonates via palladium-assisted hydrogen transfer by ammonium formate. Brunel^[14] developed the Pd/P(*t*-Bu)₃-catalyzed transfer hydrogenation of alkenes with formic acid as the

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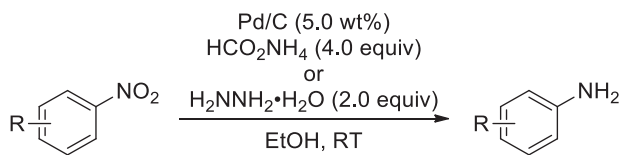
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hydrogen source and moderate-to-excellent yields were obtained in 2007. Palladium-catalyzed transfer hydrogenation of nitro compounds with CO/H₂O as the hydrogen source was reported by Krogl ^[15]. In this work, Pd(II) complexes with pyridines as catalyst showed well catalytic activity and the kinetics of this process has been studied. Subsequently, heterogenized bimetallic Pd–Pt–Fe₃O₄ nanoflakes as magnetically recyclable catalysts for chemoselective nitroarene reduction, using ammonia borane as hydrogen source, was reported by Kim et al. ^[16] Recently, Gallou et al. ^[17] reported that the sustainable and scalable Fe/ppm Pd nanoparticle-catalyzed nitro group reductions in water at room temperature using KBH₄ as the hydride source. This reduction process was suitable for a standard reaction vessel alleviating the need for specialized hydrogenation equipment.

In recent years, many novel catalysis systems and hydrogen source have been developed. For example, Corma et al. ^[8a] developed heterogeneous gold (Au/SiO₂)-catalyzed hydrogenation of α , β -unsaturated nitro compounds with H₂ for the selective synthesis of oximes. In addition, ammonia borane have attracted the attention of chemists as a hydrogen storage materials and hydrogen source. Kinjo et al. ^[11g] reported the 1,3-diazaphospholene-catalyzed transfer hydrogenation of N=N bond with ammonia borane as the hydrogen source under mild reaction conditions. Subsequently, Liu et al. ^[7c] reported cobalt-catalyzed, solvent-controlled chemodivergent transfer hydrogenation of nitriles for the synthesis of primary, secondary, and tertiary amines. The Co-pincer catalyst showed high efficiency under mild reaction conditions.

To the best of our knowledge, transition-metal-catalyzed hydrogenation or transfer hydrogenation of nitro compounds to obtain amines had opened a straightforward route to get valuable building blocks in natural products, pharmaceuticals, and fine chemical compounds. Direct hydrogenation with hydrogen gas and transfer hydrogenation are two parallel strategies for hydrogenation reactions. The catalytic hydrogenation of nitro compounds often adopts hydrogen gas as hydrogen source. Alternatively, transfer hydrogenation appeals to many chemists because it does not require the use of a flammable gas. A wide variety of H atom donors are available for use in both homo- and heterogeneous catalytic transfer hydrogenation reactions, such as formic acid, alcohols, Hantzsch esters, cyclohexenes, ammonia borane, formate, and hydrazine hydrate, etc. Stokes et al. ^[9k] found the transfer hydrogenation of alkenes and alkynes in which water was used as a stoichiometric H atom donor. Diboron reagent was found that could efficiently mediate the transfer of H atoms from water directly onto unsaturated C–C bonds using a palladium catalyst. The mechanistic experiments suggested that this reaction was made possible because a hydrogen atom was transferred from water to generate a Pd–hydride intermediate.

In addition, transition-metal-catalyzed transfer hydrogenation of nitro compounds has been a very active field. Gallagher et al. ^[18] reported a scalable chemoselective reduction of nitro compounds in the presence of an aryl imine, using (NH₄)₂S/EtOH or hydrogenation (Sponge Nickel), to afford the corresponding amino imines in moderate-to-excellent yields. The process showed well-reducible groups tolerance. The transfer hydrogenation of nitro compounds using nickel boride catalyst prepared *in situ* in nanocellulose solution with excellent yields was reported by Dinér et al. ^[19] The results indicated that nanocellulose has a stabilizing effect on the catalyst, which increased the



Scheme 1. Pd/C-catalyzed transfer hydrogenation of nitro compounds.

turnover number and enables low loading of nickel catalyst. The metal- and base-free reduction of nitro compounds was also developed by Kumar^[20] and Benaglia,^[15] respectively. According to their research, an abundantly available quinazoline alkaloid or HSiCl₃ was employed as the hydrogen source and the reaction showed wide general applicability. A highly efficient heterogeneous and reusable catalytic system always is the respectable choice. Kappe et al.^[21] reported highly active and reusable magnetic iron oxide nanocrystal-catalyzed transfer hydrogenation of nitro compounds with hydrazine hydrate as the hydrogen source. The reactions were carried out under reflux conditions in EtOH and >84% yield was obtained.

To the best of our knowledge, ammonium formate and hydrazine hydrate are the good choice as hydrogen source due to the good atom-economy and environmental friendliness. The Pd/C catalyst is also an interesting alternative to catalyze the transfer hydrogenation of nitro compounds. Herein, we reported an efficient process for the Pd/C-catalyzed transfer hydrogenation of nitro compounds using ammonium formate and hydrazine hydrate independently (Scheme 1).

In the course of our continuous research on Pd/C-catalyzed hydrogenation and transfer hydrogenation of unsaturated compounds, amines were prepared in Pd/C-catalyzed transfer hydrogenation of nitro compounds. The initial experiment began with 4-nitrotoluene (**1a**) as the model starting materials, wet Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 10 wt% wet Pd/C based on starting material **1a**) as catalyst using ammonium formate (2.0 equiv) as hydrogen source in ethanol at 60 °C. The product aniline **2a** was isolated with 71% yield (Table 1, Entry 1). This result showed that heterogeneous Pd/C can be applied to catalyze transfer hydrogenation of nitro compounds in the presence of ammonium formate. Then the temperature, solvents, catalysts and hydrogen source were evaluated to improve the efficiency of the reaction.

First, ammonium formate (4.0 equiv) was added as the hydrogen source to improve the yield and aniline was isolated only with 78% yield (Entry 2). Then the reaction was carried out at room temperature in the presence of ammonium formate (4.0 equiv) and 98% yield was obtained (Entry 3). The excellent yield indicated that the higher temperature is unfavorable for the transfer hydrogenation and the decomposition process of ammonium formate was accelerated. The yield was decreased to 88% when 3.0 equiv ammonium formate was used as the hydrogen source (Entry 4). Followed by the above results, methanol (MeOH, 87%, Entry 5), 1,4-dioxane (40%, Entry 6), and acetonitrile (56%, Entry 7) were tested as solvent to improve the yield of **2a** in Pd/C-catalyzed transfer hydrogenation of 4-nitrotoluene at room temperature. The results indicated that ethanol was the best choice in the transfer hydrogenation process.

Subsequently, the other metal salts, CuI (10 mol%), Fe(acac)₃ (10 mol%), and RuCl₃·3H₂O (5 mol%) were tested as the catalyst and no product was detected

Table 1. Conditions optimization for the transfer hydrogenation of nitro compounds.^a

Entry	Cat.(x)	Hydrogen source (y)	Solvent (T)	Yield (%) ^b
1	Pd/C (10 wt%)	HCO ₂ NH ₄ (2.0)	EtOH (60)	71
2	Pd/C (10 wt%)	HCO ₂ NH ₄ (4.0)	EtOH (60)	78
3	Pd/C (10 wt%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	98
4	Pd/C (10 wt%)	HCO ₂ NH ₄ (3.0)	EtOH (RT)	88
5	Pd/C (10 wt%)	HCO ₂ NH ₄ (4.0)	MeOH (RT)	87
6	Pd/C (10 wt%)	HCO ₂ NH ₄ (4.0)	1,4-dioxane (RT)	40
7	Pd/C (10 wt%)	HCO ₂ NH ₄ (4.0)	CH ₃ CN (RT)	56
8	CuI (10 mol%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	NA
9	Fe(acac) ₃ (10 mol%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	NA
10	RuCl ₃ ·3H ₂ O (5 mol%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	NA
11	PdCl ₂ (5 mol%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	trace
12	Pd(OAc) ₂ (5 mol%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	trace
13	Pd/C (5 wt%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	>99
14	Pd/C (2 wt%)	HCO ₂ NH ₄ (4.0)	EtOH (RT)	81
15	/	HCO ₂ NH ₄ (4.0)	EtOH (RT)	NA
16	Pd/C (5 wt%)	/	EtOH (RT)	NA
17	Pd/C (5 wt%)	HCO ₂ Na (4.0)	EtOH (RT)	NA
18	Pd/C (5 wt%)	HCO ₂ H (4.0)	EtOH (RT)	NA
19	Pd/C (5 wt%)	HCO ₂ H (4.0)/NEt ₃ (2.0)	EtOH (RT)	39
20	Pd/C (5 wt%)	H ₂ NNH ₂ ·H ₂ O (4.0)	EtOH (RT)	>99
21	Pd/C (5 wt%)	H ₂ NNH ₂ ·H ₂ O (2.0)	EtOH (RT)	>99
22	Pd/C (5 wt%)	H ₂ NNH ₂ ·H ₂ O (1.0)	EtOH (RT)	57

^aUnless other stated, all reactions are carried out with **1a** (0.5 mmol), catalyst, hydrogen source, and solvent (3.0 mL) under air at 60 °C or room temperature.

^bIsolated yields.

(Entries 8–10). To investigate whether Pd/C was the only option as the catalyst, PdCl₂ (5 mol%) and Pd(OAc)₂ (5 mol%) were evaluated independently and only trace amount of aniline was detected (Entries 11 and 12). The black palladium was formed in the reaction system and lead to the loss of the catalytic activity, which may be the principal reason. Then the loading of catalyst Pd/C was decreased to 5 wt% and 2 wt%, respectively (based on **1a**). The product aniline was isolated with >99% (Entry 13) and 81% (Entry 14) yield, respectively. These results showed that Pd/C (5 wt% based on nitro compounds) was the best choice as catalyst.

The transfer hydrogenation process could not occur without the Pd/C or ammonium formate (Entries 15 and 16). The other hydrogen sources, sodium formate, and formic acid also were not applicable for the catalytic system (Entries 17 and 18). While HCO₂H (4 equiv)/NEt₃ (2 equiv) was added into the system as hydrogen source, 39% yield of aniline was obtained (Entry 19). In order to explore broad transfer hydrogenation reagents, hydrazine hydrate (H₂NNH₂·H₂O) also was tested and showed well results (Entries 20–22, >99% yield). The optimization results showed that ammonium formate (4.0 equiv) or H₂NNH₂·H₂O (2.0 equiv) was all the best hydrogen source for Pd/C-catalyzed transfer hydrogenation of nitro compounds.

Finally, the best reaction conditions of Pd-catalyzed transfer hydrogenation of nitro compounds were obtained, using Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material **1**) as catalyst in EtOH at

Table 2. Pd/C-catalyzed transfer hydrogenation of nitro compounds.











$$\text{R-C}_6\text{H}_4\text{-NO}_2 \xrightarrow{\text{Conditions A or B}} \text{R-C}_6\text{H}_4\text{-NH}_2$$

1
2

Entry	Substrate	Product	Conditions ^a	Yield (%) ^b
1	 1a	 2a	A B	>99 >99
2	 1b	 2b	A B	90 92
3	 1c	 2c	A B	>99 >99
4	 1d	 2d	A B	>99 >99
5	 1e	 2e	A B	79 82
6	 1f	 2f	A B	>99 94
7	 1g	 2g	A B	>99 >99
8	 1h	 2h	A B	48 61
9	 1i	 2i	A B	>99 91
10	 1j	 2j	A B	NA >NA
11	 1k	 2k	A B	>99 >99
12	 1l	 2l	A B	85 >99
13	 1m	 2m	A B	38 56
14	 1n	 2n	A B	NA NA
15	 1o	 2o	A B	NA NA

(continued)

Table 2. Continued.

Entry	Substrate	Product	Conditions ^a	Yield (%) ^b
16	 1p	 2n	A ^c B ^d	>99 >99
17	 1q	 2q	A B	>99 >99
18	 1r	 2r	A B	>99 >99
19	 1s	 2s	A B	>99 >99
20	 1t	 2q	A B	>99 >99

^aReaction conditions **A**: **1** (0.50 mmol), Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material **1**), HCO₂NH₄ (126 mg, 2.0 mmol, 4.0 equiv), EtOH (3.0 mL), RT, 12 h; reaction conditions **B**: **1** (0.50 mmol), Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material **1**), H₂NNH₂·H₂O (50 mg, 1.0 mmol, 2.0 equiv), EtOH (3.0 mL), RT, 12 h.

^bIsolated yield.

^cHCO₂NH₄ (252 mg, 4.0 mmol, 8.0 equiv) was used.

^dH₂NNH₂·H₂O (100 mg, 2.0 mmol, 4.0 equiv).

room temperature with ammonium formate (4.0 equiv) or H₂NNH₂·H₂O (2.0 equiv) as hydrogen source.

Under the optimal conditions, a variety of nitro compounds **1a–t** were subjected to the Pd/C-catalyzed transfer hydrogenation, as shown in Table 2. For the nitro compounds **1a–f** (Table 2, Entries 1–6) with different substituents, –CH₃, –Et, –OCH₃, –OH, and –NH₂, on the *para*-position of nitro group, carried out under the optimal reaction conditions **A** and **B**, moderate-to-excellent isolated yields (79% to >99% yield) of **2a–f** were achieved, respectively. The relatively lower yield was obtained when the substrate 4-nitrophenol was with stronger electron-donating substituent –OH. The reaction system could also be applied for the transfer hydrogenation of substrates **1g**, **1i**, **1k**, **1l**, **1p–1t**, with *ortho*- or *meta*- substituents, and obtain the excellent yields (Entries 7, 9, 11–12, 16–20).

Unfortunately, when the nitro substrates bearing *ortho*- or *meta*-chloro substituent (Entries 8 and 13), only 38% and 61% target products were isolated due to the dechlorination product aniline was formed and detected. In the transfer hydrogenation of 2-nitrophenol **1j**, 3-nitroaniline **1n**, 3-nitrophenol **1o**, no product was detected and the starting material were recovered (Entries 10, 14, and 15). The reason was speculated that these substrates with electro-donating groups –NH₂ and –OH would lead to the lower reductive activity of starting materials. In addition, the *m*-dinitrobenzene could be reduced to *m*-diaminobenzene and it may be because hydroxylamine was formed as intermediate and the reductive process from nitro to hydroxylamine was the rate controlling step (Entry 16). Hence, the *m*-nitro group showed less influence on the transfer hydrogenation process.

Table 3. Test of scale-up conditions and recycling of Pd/C catalyst.^a

Recyclable times	m (Pd/C) (g)	m (1a) (g)	m (2a) (g)	Yield (%) ^b
First	0.50	10.0	7.7	98.0
Second	0.45	9.0	6.8	95.3
Third	0.45	9.0	6.3	87.2

^a1a (1.0 equiv), Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material 1a), H₂NNH₂·H₂O (2.0 equiv), EtOH (100 mL), RT, 12 h.

^bIsolated yields.

In order to test the effect of Pd/C-catalyzed transfer hydrogenation of nitro compounds under scale-up conditions, 4-nitrotoluene **1a** (10.0 g) was input into the reaction with hydrazine hydrate as hydrogen source. The target product **2a** was attained with 98.0% yield (Table 3, Entry 1). The recycle time of Pd/C catalyst was also tested under the standard reaction conditions. Pleasingly, the catalytic activity of Pd/C catalyst had decreased slightly at second and third utility (Entries 2 and 3, 95.3% and 87.2%). The result indicated that the reaction system composed of recyclable Pd/C catalyst and hydrazine hydrate may be appropriate for the scale-up and industry production of amines.

In summary, the Pd/C-catalyzed transfer hydrogenation of nitro compounds was successfully developed using ammonium formate or hydrazine hydrate as hydrogen source at ambient temperature. The process afforded amines with up to >99% yield. The catalysis system of these reactions will provide a powerful means to develop new applications for Pd/C-catalyzed reduction of C=O, C=N, C=N and aromatic compounds with ammonium formate or hydrazine hydrate as hydrogen source.

Experimental section

General methods

All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200–300 mesh). The chemical shifts (δ) of the ¹H NMR (400 MHz) signals are reported in ppm relative to tetramethylsilane (TMS) and by employing the residual solvent resonance as the internal standard. Data are reported in the following order: chemical shift, multiplicity [s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet)], coupling constants (Hz), and integration. The chemical shifts (δ) of the ¹³C NMR (100 MHz) signals are reported in ppm relative TMS and by employing the solvent resonance as the internal standard.

Procedure A

A mixture of nitro compounds **1** (0.50 mmol) and Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material **1**) in EtOH

(3 mL) was added into a Schlenk flask (25 mL) and stirred at room temperature. Followed by addition of HCO_2NH_4 (126 mg, 2.0 mmol, 4.0 equiv) and the mixture was stirred at room temperature until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

Procedure B

A mixture of nitro compounds **1** (0.50 mmol) and Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 5 wt% wet Pd/C based on starting material **1**) in EtOH (3 mL) was added into a Schlenk flask (25 mL) and stirred at room temperature. Followed by addition of $\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$ (50 mg, 1.0 mmol, 2.0 equiv) and the mixture was stirred at room temperature until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

p-toluidine (2a)

Yield **A**: >99%, 54.3 mg, **B**: >99%, 54.6 mg, white solid. ^1H NMR (400 MHz, CDCl_3) δ 6.96 (d, $J=7.9$ Hz, 2H), 6.62–6.60 (m, 2H), 3.23 (brs, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 129.7, 127.8, 115.3, and 20.5.

Funding

The work was supported by the Youth Science and Technology Talent Development Project in Education Department of Guizhou Province [grant number qianjiaohe KY zi [2017] number 261], the Union Foundation of Science and Technology Department of Guizhou Province [grant number qiankehe LH zi [2015] number 7614], and Innovation Team of Liupanshui Normal University [grant number LPSSYKJTD201601].

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