



Chemoselective hydrogenation of nitrobenzyl ethers to aminobenzyl ethers catalyzed by palladium–nickel bimetallic nanoparticles



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ABSTRACT

A highly efficient and chemoselective hydrogenation of nitrobenzyl ethers to aminobenzyl ethers was developed by using a novel palladium–nickel bimetallic nanocatalyst. Since the catalytic selectivity was resulted from the synergistic effects between two metals rather than the traditional catalyst poisons, the hydrogenation proceeded smoothly under additive-free conditions. Thus, the work-up procedure was as simple as to recover the catalyst by a magnetic separation and then to evaporate the solvent.

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1. Introduction

In the past decade, the compounds containing the subunit of aminobenzyl ether **1** have been found as important applications in organic synthesis, drug discovery and material sciences. As shown in Fig. 1, iteamine (*o*-aminobenzyl β-D-glucopyranoside) is a natural product isolated recently from *itea virginica*.¹ The compound SB1578 (as a potent inhibitor of JAK2/FLT3 at phase I clinical trials) is developed for the treatment of rheumatoid arthritis.² 3,5-Bis(methoxymethyl)-aniline is a main building block for the synthesis of the cationic dendrons in the discovery of dye-sensitized solar cells.³

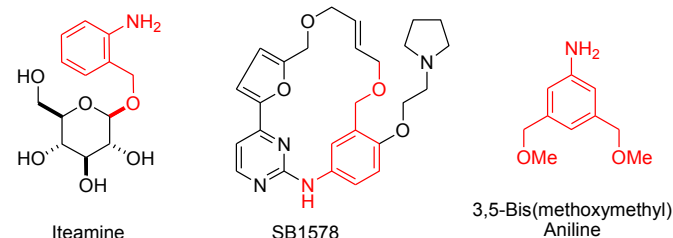
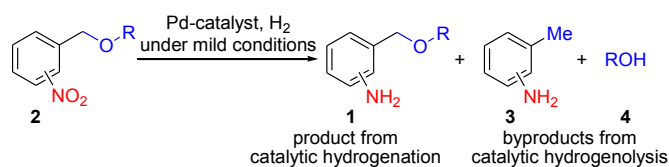


Fig. 1. Some important aminobenzyl ethers.

In literature, aminobenzyl ethers **1** are routinely synthesized by chemoselective reduction of the corresponding nitrobenzyl ethers **2**. Investigation showed that Pd-catalyzed hydrogenation is the most efficient, convenient and clean method to convert nitrobenzenes into anilines in laboratories.⁴ But, the most often used methods for the transformation of **2** to **1** are catalytic transfer hydrogenation⁵ and dissolving metal reduction.⁶ As shown in Scheme 1, this situation was caused by the fact that Pd-catalysts also have a strong ability to catalyze the hydrogenolysis⁷ of benzyl ethers under similar conditions for the hydrogenation of nitrobenzene. Thus, low chemoselectivity and efficiency were obtained often in the Pd-catalyzed hydrogenation of nitrobenzyl ethers **2**.⁸



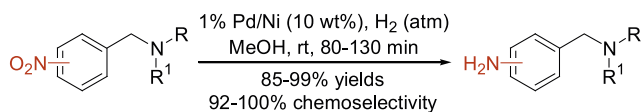
Herein, we would like to report a novel palladium–nickel bimetallic nanocatalyst, by which highly chemoselective and efficient hydrogenation of **2** to **1** was achieved under room temperature and atmospheric pressure.

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2. Results and discussion

In routine organic synthesis, Pd-catalyzed hydrogenolysis of benzyl ethers is so efficient that it is a major method for O-debenzylation when benzyl ether served as a protective group for alcohols or phenols.⁹ Therefore, much less attention was paid to inhibit this transformation in literature. In a few methods that dealt specifically with this purpose,¹⁰ amines were used as poisons for the Pd-catalysts with two characteristics: (a) aliphatic amines were suitable poisons, but aromatic amines were not; (b) the hydrogenolysis of alkyl benzyl ethers could be inhibited, but aryl benzyl ethers could not. Therefore, it is necessary to develop new catalysts and general processes for the chemoselective hydrogenation of **2** to **1**.

In recent years, the catalytic applications of bimetallic nanoparticles have made great progress.¹¹ Since the formation of heterometallic bonds and the changes of average metal–metal bond lengths, bimetallic nanoparticles have typically shown different electronic effect (or ligand effect) and geometric effect (or strain effect) from their parent metals. In our recent work,^{12a} a novel 1% Pd/Ni (containing 1 wt% of Pd) bimetallic nanoparticle was prepared by simply boiling the mixture of Na₂PdCl₄ and Raney-Ni in water. As shown in Scheme 2, when it was used as a catalyst, nitrobenzylamine was chemoselectively hydrogenated to the corresponding aminobenzylamine based on its synergistic effects.



Scheme 2. Chemoselective hydrogenation of nitrobenzylamines.

Thus, we were encouraged to test further the catalytic selectivity of this Pd/Ni bimetallic nanocatalyst in the hydrogenation of nitrobenzyl ethers. As shown in Table 1, 4-methylphenyl 4-nitrobenzyl ether (**2a**) was chosen as a model substrate due to the fact that phenyl benzyl ether is highly sensitive to Pd-catalyzed hydrogenolysis. Under room temperature and atmospheric pressure, the desired product **1a** was obtained in 71% yield and 75% chemoselectivity over Pd/C catalyst (entry 1). By using Raney-Ni as a catalyst, the hydrogenation stopped automatically within 3 h to give **1a** in 55% yield with recovery of **2a** in 41% yield (entry 2).

Table 1
Hydrogenations of **2a** by using different catalysts^a

Entry	Catalyst (wt %)	Net weight of metal (mg)	Pressure (psi)	Time (h) ^b	Yield of 1a (%) ^c	Selectivity of 1a (%) ^d
1	5% Pd/C (5)	Pd (0.61)	—	1	71	75
2	Raney-Ni (50)	Ni (122)	—	3	55	100
3	1% Pd/Ni (50)	Pd (1.22), Ni (122)	—	1	93	95
4	1% Pd/Ni (30)	Pd (0.73), Ni (73)	—	1.5	98	100
5	1% Pd/Ni (20)	Pd (0.49), Ni (49)	—	4.5	91	100
6 ^e	1% Pd/Ni (20)	Pd (0.49), Ni (49)	45	4.5	98	100
7 ^e	1% Pd/Ni (10)	Pd (0.24), Ni (24)	45	6	90	100
8 ^e	1% Pd/Ni (10)	Pd (0.24), Ni (24)	90	6	98	100

^a A mixture of **2a** (1 mmol) and catalyst in MeOH (10 mL) was stirred under H₂ at room temperature and atmospheric pressure (on an atmospheric pressure hydrogenation apparatus).

^b The time is when the absorption of hydrogen ceased automatically except for the hydrogenation in entry 1.

^c Isolated yield was obtained.

^d It was determined by ¹H NMR spectra of the crude products.

^e The experiments proceeded on a Parr-hydrogenator.

However, **1a** was obtained in 93% yield and 95% chemoselectivity in the presence of 50 wt% of the Pd/Ni bimetallic catalyst (entry 3). Much higher chemoselectivity was achieved even though the amount of palladium metal (net weight) in entry 3 was used more than that in entry 1. To our delight, quantitative yield and chemoselectivity of **1a** were obtained in the presence of 30 wt% of Pd/Ni bimetallic catalyst (entry 4). The results in entries 5–8 indicated that the chemoselectivity was not influenced by using lower ratios of Pd/Ni bimetallic catalyst, but the conversion was decreased and prolonged times were required. However, these problems can be solved easily by increasing the hydrogen pressure a little.

As shown in Table 2, the catalytic activity of the Pd/Ni bimetallic catalyst was influenced significantly by the reaction solvents. The all tested alcohols proved to be excellent solvents for this hydrogenation (entries 1–3) and MeOH was the best one (entry 1). We interestingly observed that the Pd/Ni bimetallic nanoparticles were all attracted to the surface of the standing magnetic stirring bar in the alcohol solvents. After the magnetic stirring bar was spinning, the nanoparticles were dispersed fully into the alcohol solvents. However, only parts of nanoparticles were dispersed into the non-alcohol solvents (entries 4–7) and most of them were still attracted to the surface of the spinning magnetic stirring bar.

Since nickel metal is ferromagnetic, the Pd/Ni bimetallic nanoparticles could be recovered conveniently by use of a magnetic stirring bar (a magnetic separation) in work-up procedure and re-used in the subsequent rounds. As shown in Table 3, a recycling study shows that the catalytic activity of the Pd/Ni bimetallic catalyst decreased steadily (entries 1–4). Although the chemoselectivity was not influenced in the fourth round, the conversion could not be completed even prolonged reaction time was used (entry 4). These results may be caused by the fact that some of palladium metals were peeled off from the surface of the Pd/Ni bimetallic nanoparticles in each round. Thus, they were converted from ‘the magnetic palladium’ into ‘the non-magnetic palladium’ and were lost in the work-up procedures by a magnetic separation. The ICP analyses of the catalyst after fourth round also showed that the percentage of palladium is 0.74%, which gave a strong support to our hypothesis.

Finally, the scope was tested by using different substrates as shown in Scheme 3. Although the aryl benzyl ethers (R=aryl) were extremely sensitive to hydrogenolysis, excellent yields and chemoselectivity were obtained for the conversion of **2a–2j** into **1a–1j**. No influence was observed for the substituted position of the nitro-group on the benzene ring (**1a–1c**). It seemed that the

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