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Selective Hydrogenation of Nitroaromatic Compounds with a Nickel-Oxide-Supported Nano-Palladium Catalyst under Ambient Reaction Conditions

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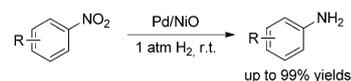
The chemoselective hydrogenation of nitrobenzene and its derivatives is one of the most important industrial reactions for the production of their corresponding amines,^[1] which are versatile intermediates and precursors in the preparation of pharmaceuticals, agrochemicals, pigments, dyes, polymers, and other fine chemicals.^[2] Traditional methods for the synthesis of nitrobenzene derivatives involve the use of stoichiometric reducing agents, such as sodium hydrosulfite, iron, tin, and zinc.^[3] Currently, the catalytic hydrogenation of nitrobenzene is the main process for the synthesis of anilines in the chemical industry.^[4] Over the past few decades, numerous methods have been developed for the synthesis of amines, the search for facile, chemoselective, cost-effective, and environmentally friendly processes that avoid the use of expensive and hazardous stoichiometric reducing agents in a large excess or for performing the hydrogenation reactions under mild conditions remains a challenge.

Transition-metal catalysts (based on Pt, Pd, Ru, etc.)^[5] have shown high catalytic activities for the hydrogenation of nitrobenzenes; however, sometimes it is difficult to achieve the selective hydrogenation of nitro substrates that contain other reducible groups with these catalysts. Other metal catalysts, such as Au, Ag, Cu, etc., have typically shown low activities and require harsh reaction conditions.^[1, c, 6] Several heterogeneous catalysts are commercially available for the chemoselective hydrogenation of nitroarenes. Excellent chemoselectivity was achieved in polar solvents by using a Pt/C catalyst that was modified with soluble vanadium compounds as additives by using H₃PO₂,^[7] but the amount of the modifying agent must be precisely controlled.^[3] Corma and co-workers^[3a, 8] reported that gold nanoparticles that were supported on TiO₂ or Fe₂O₃ catalyzed the chemoselective hydrogenation of functionalized nitroarenes with H₂ under relatively mild conditions, thereby opening up a route for performing these reactions in environ-

mentally sustainable processes. In general, widely differing reaction conditions are used but very few catalysts^[6c, 9] are able to catalyze the reduction reactions under ambient conditions.

Herein, we report the preparation, characterization, and an exploration of the catalytic performance of a nickel-oxide-supported nano-palladium catalyst, that is, Pd/NiO-M, in the chemoselective hydrogenation of nitrobenzene derivatives under ambient reaction conditions (Scheme 1).

The NiO (NiO-M) support was prepared by the sol-gel polymerization of resorcinol and formaldehyde with Ni(NO₃)₂·6H₂O



Scheme 1. Selective hydrogenation of nitrobenzenes under ambient conditions.

as an additive. A hybrid material of nickel-doped carbon aerogel was obtained after hydrothermal treatment and carbonization at elevated temperatures under a flow of nitrogen. Next, the hybrid material was treated under a flow of oxygen, thereby affording magnetic NiO. Subsequently, the Pd/NiO-M catalyst was prepared by using a sol-immobilization method. In a typical procedure, H₂PdCl₄ was reduced in distilled water by using NaBH₄ in the presence of PVA (polyvinyl alcohol) and then NiO-M was added. The nano-palladium particles were deposited onto the NiO-M support and the Pd/NiO-M catalyst was obtained after washing three times with distilled water. For comparison, an immobilized nano-Pd catalyst on a commercial NiO support (NiO-C) was also prepared by using the same procedure and is denoted as Pd/NiO-C.

To explore the structures of the Pd/NiO-M and Pd/NiO-C catalysts, they were characterized by using X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), TEM, X-ray photoelectron spectroscopy (XPS), and BET surface-area analysis. The XRD diffraction patterns suggested that the major crystal structure of NiO-C should contain NiO(111), (200), (220), (311), and (222) lattices (PDF-78-0643). The XRD diffraction patterns of NiO-M suggested that it was a better-crystallized structure and obvious Ni(111), (200), and (220) peaks were observed (PDF-87-0712). The introduction of palladium didn't change the crystal structure of NiO; both the NiO-M and NiO-C supports showed almost the same XRD diffraction patterns as that of pure NiO. Moreover, there was no observable peak for palladium, which suggested that

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the palladium species were highly dispersed over the NiO support.

Next, the catalysts were characterized by using TEM and HR-TEM (Figure 2), which suggested that the average size of the palladium particles in Pd/NiO-M was about 5 nm. The Pd(111) crystal lattice can be clearly observed from the HR-TEM picture. Interestingly, it is difficult to see the palladium particles on the Pd/NiO-C catalyst, although the NiO(111) lattice can be observed. This result may be owing to the low loading of palladium.

The XPS spectra supported the XRD and TEM observations (Figure 3). For Pd/NiO-M, the typical binding energies of NiO (854.3 eV) and Pd (335.4 eV) were observed. Conversely, only NiO (854.3 eV) was observed for Pd/NiO-C; in this case, the signal for Pd was too weak to be determined. Taken together with the TEM data, we imagined that the palladium species were dispersed within the NiO particles in Pd/NiO-C and, therefore, they could not be seen by TEM and XPS.

The catalytic activity of the NiO-immobilized palladium catalysts was explored by using the hydrogenation of 1-methyl-4-nitrobenzene as a model reaction (Table 1). Clearly, Pd/NiO-M showed the highest activity for the hydrogenation of 1-methyl-4-nitrobenzene, thus affording *p*-methylaniline in quantitative yield with a palladium loading of 0.2 mol% (Table 1, entry 1). However, the commercial-NiO-supported Pd, that is, Pd/NiO-C, only gave trace levels of conversion under the same reaction conditions (Table 1, entry 2). To more reasonably compare the activities of these supported catalysts, 60 mg Pd/NiO-C was used for the catalytic hydrogenation of 1-methyl-4-nitrobenzene. In this case, the palladium loading was 0.24 mol%, which was even higher than that that on Pd/NiO-M. However, again, only trace amounts of *p*-methylaniline were detectable (Table 1, entry 3).

Next, the scope and limitations of Pd/NiO-M with a range of structurally diverse nitroaromatics were examined. As shown in Table 2, Pd/NiO-M exhibited high catalytic activity for the hydrogenation of nitrobenzene with complete conversion (Table 2, entry 1). Then, the catalytic hydrogenation reactions of nitrobenzene derivatives that contained various electron-donating and electron-withdrawing groups were performed. Clearly, the presence of a methyl group at different positions on the phenyl ring afforded the corresponding aniline in excellent yields (Table 2, entries 2–4). The introduction of electron-donating groups remarkably retarded the hydrogenation reaction, although good yields were also obtained with longer reaction times. For example, quantitative yields were obtained if *m*- and *p*-methoxynitrobenzene were used as starting materials (Table 2, entries 5 and 6). Moreover, the hydrogenation reactions of *m*- and *p*-chloronitro-

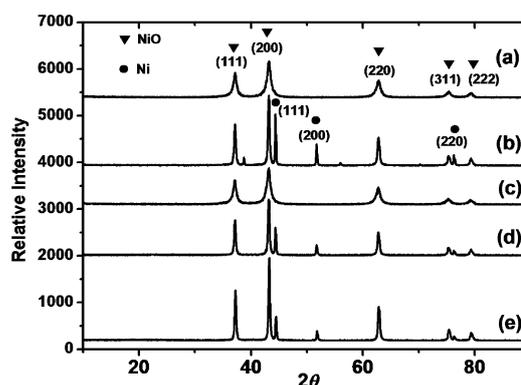


Figure 1. XRD diffraction patterns of a) NiO-C, b) NiO-M, c) Pd/NiO-C, d) Pd/NiO-M, and e) Pd/NiO-M after five runs.

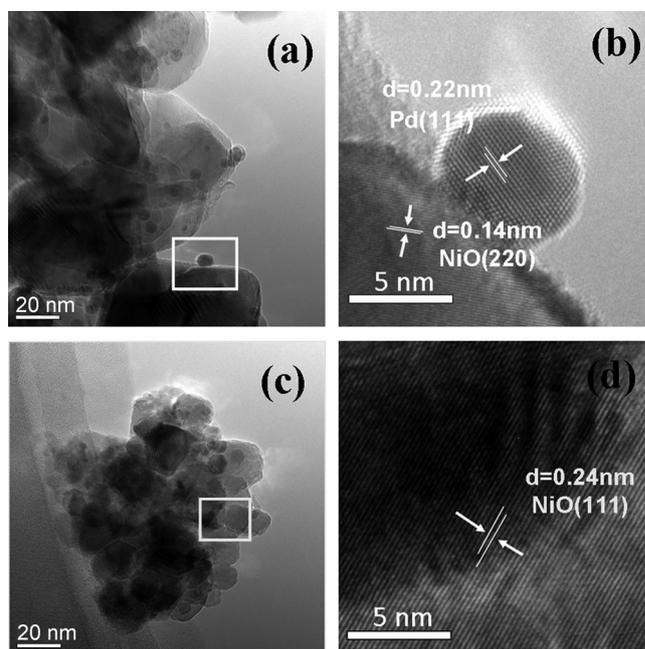


Figure 2. TEM and HR-TEM pictures of Pd/NiO-M (a, b) and Pd/NiO-C (c, d).

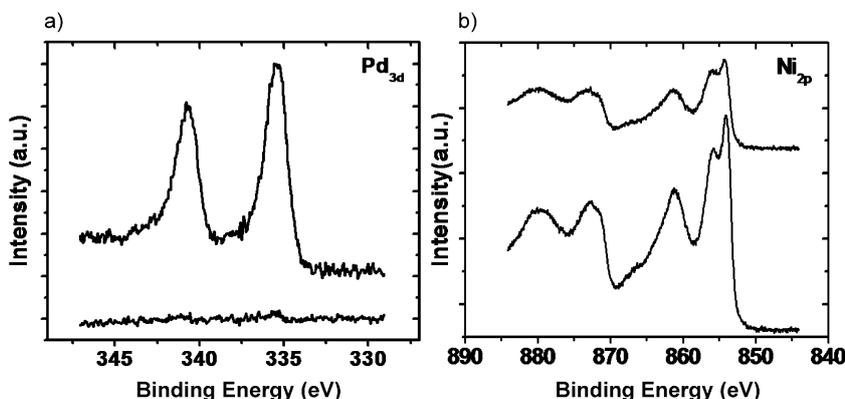
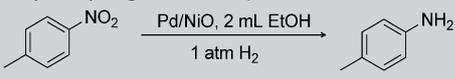


Figure 3. XPS spectra of a) Pd 3d of Pd/NiO-M (top) and Pd/NiO-C (bottom) and b) Ni 2p of Pd/NiO-M (bottom) and Pd/NiO-C (top).

Table 1. Catalytic hydrogenation of *p*-Me-nitrobenzene into aniline.^[a]



Entry	Catalyst [mol%]	Conversion [%] ^[b]	Yield [%] ^[b]
1	Pd/NiO-M (0.2)	> 99	> 99
2	Pd/NiO-C (0.07)	trace	trace
3 ^[c]	Pd/NiO-C (0.24)	trace	trace

[a] Reaction conditions: 1-Methyl-4-nitrobenzene (1.0 mmol), catalyst (20 mg), EtOH (2 mL), H₂ balloon, 25 °C, 1 h. [b] Conversions and yields were determined by GC-FID with biphenyl as an external standard. [c] Pd/NiO-C was used (60 mg); in this case, the amount of palladium that was used was the same as that in entry 1.

benzene were performed. Disappointingly, the hydrodechlorination reaction occurred, despite their complete conversion. The yields of the target products were 72% and 83%, respectively (Table 2, entries 7 and 8). Hydroxy, sulfonyl, amino, and nitro groups were well-tolerated in the hydrogenation of nitro compounds, catalyzed by Pd/NiO-M, into their corresponding amines in almost-quantitative yields within 3–10 h (Table 2, entries 9–14). In the case of 1-nitronaphthalene and 2-nitronaphthalene, Pd/NiO-M showed high catalytic activity for the hydrogenation reaction in >99% yield at 40 °C (Table 2, entries 15–16). Interestingly, the hydrogenation of 2,6-di-methylnitrobenzene was more difficult: It required 60 °C for 12 h (Table 2, entry 17). The low activity of 2,6-di-methylnitrobenzene might be caused by the steric hindrance of the methyl groups.

The selective hydrogenation of nitrobenzene derivatives in the presence of other reducible groups is also of interest. First, a nitrobenzene with an aldehyde substituent was tested. To our delight, 4-nitrobenzaldehyde was quantitatively hydrogenated into 4-aminobenzaldehyde without reducing the aldehyde group (Table 3, entries 1). Furthermore, other reducible groups, such as carboxy and ketone groups, were tolerated, with the quantitative conversion of the nitrobenzenes into the desired products (Table 3, entries 2 and 3). However, if 1-nitro-3-vinylbenzene was used as the starting material, the vinyl group could be completely hydrogenated and 3-ethylnitrobenzene was generated in qualitative yield.

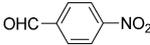
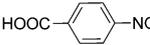
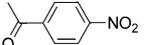
After the completion of the exploration of the catalytic performance of Pd/NiO-M, the reusability of the catalyst was tested. After the reaction, the catalyst was separated by centrifugation and washed with distilled water, followed by drying in air at 80 °C. The catalyst was used in five successive cycles in the hydrogenation of 1-methyl-4-nitrobenzene and 85% yield was maintained for the 5th run (Figure 4). To find out the reason for the decreasing catalytic activity, the catalyst was characterized by XRD and ICP-AES after its use in five runs. According to the XRD results (Figure 1e), no diffraction pattern for palladium was observable, which suggested that the palladium species remained highly dispersed. However, according to ICP-AES analysis, the palladium loading decreased from 1.1 wt.% to 0.8 wt.%. Therefore, the deactivation of the catalyst may be caused by palladium leaching during the reaction.

Table 2. Selective hydrogenation of nitroaromatic compounds with a Pd nanocatalyst.^[a]

Entry	Substrate	T [°C]	t [h]	Yield [%] ^[b]
1		25	1	> 99
2		25	1	> 99
3		25	1	> 99
4		25	1	> 99
5		25	3	> 99
6		25	5	> 99
7		25	2	72 ^[c]
8		25	2	83 ^[c]
9		40	6	95
10		40	6	98
11		40	6	> 98 ^[d]
12		25	3	98
13		25	6	98
14		25	10	98
15		40	10	> 98 ^[d]
16		40	3	> 98 ^[d]
17		60	12	99

[a] Reaction conditions: Substrate (1.0 mmol), Pd/NiO-M (20 mg, 1 mol%), H₂ balloon, RT. [b] Yields were determined by GC-FID with biphenyl as an external standard. [c] The byproduct is aniline. [d] Yield of isolated product.

In summary, we have introduced a new procedure for the reduction of aromatic nitro compounds into amines under ambient conditions. The Pd/NiO-M catalytic material exhibited high activity and excellent chemoselectivity in the selective hydrogenation of nitrobenzenes into their aniline derivatives. This method may allow the preparation of nanocatalytic materials with specific activities and chemoselectivities and it may be of use for the development of practical nitrobenzene-hydrogenation catalysts.

Entry	Nitrobenzene	T [°C]	t [h]	Yield [%] ^[b]
1		25	2	95 ^[c]
2		40	6	> 98
3		25	2	> 99

[a] Reaction conditions: Substrate (1.0 mmol), Pd/NiO-M (20 mg, 1 mol%), H₂ balloon, RT. [b] Yield of isolated product. [c] Yields were determined by GC-FID with biphenyl as an external standard.

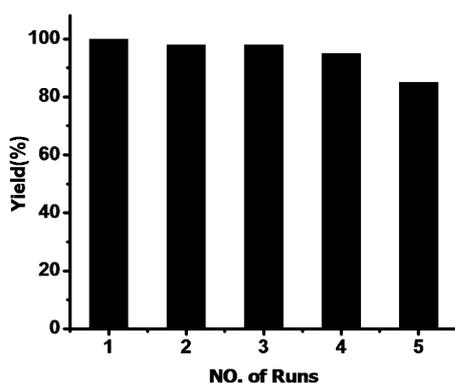


Figure 4. Recyclability of the Pd/NiO-M catalyst in the hydrogenation of 1-methyl-4-nitrobenzene.

Experimental Section

Preparation of the NiO-M nanoparticles

The NiO-M support was prepared by the sol-gel polymerization of resorcinol and formaldehyde, with Na₂CO₃ as a catalyst and 50% Ni-doped monolithic carbon aerogels. Typically, resorcinol (2.20 g, 20 mmol), formaldehyde (3.25 g, 40 mmol, 36.5% in water, MeOH-stabilized), and distilled water (6 mL) were added into a PTFE autoclave (100 mL) and the mixture was stirred for 0.5 h. Subsequently, an aqueous solution of Ni(NO₃)₂·6H₂O (5.8 g) was added dropwise and a 0.9 M solution of Na₂CO₃ (4 mL) was added into the mixture. After vigorous stirring for 1 h, the autoclave was sealed and kept at 80 °C for 1 day. Then, the autoclave was cooled to RT. The wet gels were placed into a round-bottomed flask and vacuum dried at 130 °C for 3 h. After pyrolysis at 800 °C (heating rate: 5 °C min⁻¹) for 5 h under a flow of nitrogen (20 mL min⁻¹), a black solid (about 7 g) was obtained. Then, the black solid was treated at 500 °C for 5 h in a flow of oxygen (20 mL min⁻¹) to afford the NiO-M nanoparticles (about 4.1 g).

Preparation of the Pd/NiO-M and Pd/NiO-C catalysts

Pd that was supported on NiO-M was prepared according to a sol-immobilization method. The detailed procedure for the preparation of the 1.1 wt.% Pd/NiO-M catalyst is described below. An aqueous solution of H₂PdCl₄ (0.067 mL, 35 mg mL⁻¹) was added to distilled water (5 mL). Then, an aqueous solution of PVA (1.2 mL; 5 mg mL⁻¹) was added. After 30 min, a freshly prepared 0.1 M solution of NaBH₄ (NaBH₄/Pd, 4:1 mol/mol) was added to form a dark-

brown sol. After 30 min of sol generation, the colloid was immobilized by adding NiO-M powder (100 mg). The solution was acidified to pH 1 by the addition of sulfuric acid under strong conditions and stirred for a further 2 h. The resulting solid was washed with distilled water (3 × 40 mL) and dried in air at 80 °C for 2 h to afford the Pd/NiO-M catalyst. Another catalyst, Pd/NiO-C, was prepared by using commercial NiO-C as a support. The palladium loadings for Pd/NiO-M and Pd/NiO-C were 1.1 wt.% and 0.4 wt.%, respectively, according to ICP-AES analysis.

Typical procedure for the hydrogenation of 1-methyl-4-nitrobenzene

1-Methyl-4-nitrobenzene (1.0 mmol), the catalyst (20 mg), and EtOH (2 mL) were added into a glass tube (50 mL). Then, it was exchanged with H₂ and the reaction was continued in the presence of H₂ at atmospheric pressure (H₂ balloon) at 25 °C for 1 h. After the reaction, biphenyl (150 mg) and EtOH (10 mL) were added for quantitative analysis.

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Keywords: hydrogenation • nanostructures • nickel • palladium • supported catalysts

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