

Nanocrystalline Magnesium Oxide-Stabilized Palladium(0): An Efficient and Reusable Catalyst for Selective Reduction of Nitro Compounds

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Abstract: An efficient, mild and selective synthesis of aromatic and aliphatic amines from the corresponding nitro compounds has been realized by using a ligand-free heterogeneous nanocrystalline magnesium oxide-stabilized palladium(0) catalyst, employing molecular hydrogen as the reductant. The catalyst is recovered quantitatively by simple filtration and was reused for several cycles with consistent activity.

Keywords: amines; molecular hydrogen; nanocrystalline magnesium oxide; nitro group; palladium(0); reduction

Organic amines are important starting materials for the manufacture of a variety of chemicals such as dyes, pharmaceuticals, agrochemicals, surfactants, pesticides and polymers etc.^[1] The selective reduction of nitro compounds to amines is a synthetically important transformation for the synthesis of valuable starting materials and intermediates.^[2] Furthermore, amino groups can easily be replaced by other groups (H, F, Cl, Br, I, OH etc.) *via* the corresponding diazonium salts.^[3]

A variety of reagents have been reported for the reduction of nitro compounds to the corresponding amines.^[4] Among them, the conventional and still important method is the reduction with iron and hydrochloric acid or acetic acid.^[5] Other dissolving metals such as zinc or tin in the presence of hydrochloric acid have also been used.^[6] But these processes present difficulties in product isolation from the metal sludge formed during the reaction and hence leading to disposal problems.^[7]

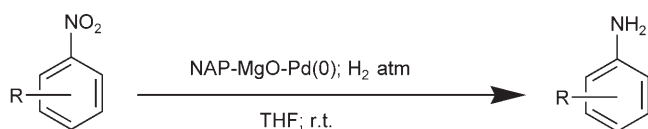
In order to avoid these drawbacks of the conventional methods, a number of heterogeneous catalysts

has been reported in recent years.^[8] These catalysts offer several advantages over their homogeneous counterparts with respect to recovery, recycling, as well as minimization of undesired toxic wastes. Baralt and Holy reported the reduction of nitrobenzene to aniline using polymer-anchored anthranilic acid-palladium complexes under high pressures of 500–800 psi at 70–100 °C.^[9] Palladium on charcoal catalyzes the reduction of nitro compounds using triethylammonium formate as the hydrogen source at reflux temperature.^[10] Hydrogenation of mono- and polynitroaromatics is realized in high yields by Pd/C catalyst *via* hydrogen transfer from cyclohexene in ethanol under reflux conditions.^[11] Recently, Shi et al. have reported the reduction of nitroarenes over nickel-iron mixed oxide catalyst using hydrazine hydrate under reflux conditions.^[12] Thus, high temperatures, pressures and longer reaction times accompany these methods of reduction of the nitro compounds.

We have earlier reported the reduction of nitroaromatic compounds using an MCM-silylamine palladium(II) catalyst^[13] and Suzuki and Stille cross coupling reactions^[14] by using a highly basic nanocrystalline magnesium oxide-stabilized palladium(0) catalyst [NAP-Mg-Pd(0)].

In continuation of our earlier work, herein we report the reduction of a variety of aromatic and aliphatic nitro compounds to the corresponding amines at ambient temperatures in good to excellent yields by using ligand-free nanocrystalline magnesium oxide-stabilized palladium(0) catalyst with molecular hydrogen as the reductant (Scheme 1).

In an endeavor to identify the best catalytic system for the reduction of nitro compounds various supported palladium catalysts were screened using nitrobenzene as the model substrate and the results are presented in Table 1. In order to obtain counterionic stabilization of PdCl₄, NAP-MgO, MgLaO, and SiO₂ were treated with Na₂PdCl₄ to afford NAP-Mg-PdCl₄,



R = any substituent

Scheme 1. Reduction of nitroarenes.

Table 1. Comparative study of different supported palladium catalysts for the reduction of nitrobenzene.^[a]

Entry	Catalyst	Time [h]	Conversion [%] ^[b]
1	Pd-MgO	2.0	98
2	PdMgLaO	2.0	70
3	Pd-C	2.0	15
4	Pd-SiO ₂	2.0	6

^[a] Reaction conditions: nitrobenzene (1 mmol), catalyst (0.015 g), dry THF (4 mL), room temperature, under H₂ atmosphere.

^[b] Determined by GC.

MgLa-PdCl₄ and Si-PdCl₄. These precursors were reduced with an excess of hydrazine hydrate to produce NAP-Mg-Pd(0). In the reaction with NAP-MgO [surface area (SA) 600 m²g⁻¹] and MgLaO (SA 37.6 m²g⁻¹), the entire amount of Na₂PdCl₄ used was consumed as detected by atomic absorption spectroscopy (AAS). On the other hand, a small amount (<0.5%) of palladate was detected by AAS in the treated sample of SiO₂ (SA 250 m²g⁻¹). In the reaction of Na₂PdCl₄ with NAP-MgO, the Na⁺ ion will interact with the O^{x-} sites/anionic vacancies and the PdCl₄²⁻ will interact with the Mg²⁺ sites/cationic vacancies present on corners or edges of nanocrystalline MgO to form the catalyst as described in Scheme 2.^[15,16]

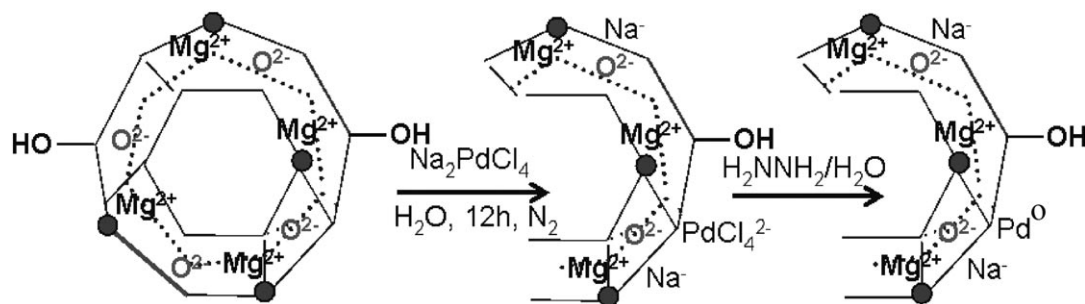
Among the different catalysts screened, [NAP-Mg-Pd(0)] provided the optimum results (Table 1, entry 1). The greater reactivity of the [NAP-Mg-Pd(0)] can be explained by the structural features of the nanocrystalline magnesium oxide as support. The enhanced activity of this catalyst over the different

supported palladium catalysts screened as well as its homogeneous counterparts, results from the high basicity and surface area of nanocrystalline magnesium oxide {aerogel-prepared MgO, NAP-MgO [specific surface area (SSA): 600 m²g⁻¹] support}. The presence of edge-corner and other defect sites allows the nanostructured MgO materials to possess a high concentration of reactive surface ions. The reactive sites on the surface of MgO are as follows: 1) the Mg²⁺ site, which is of the Lewis acid type, 2) the O²⁻ site which is of the Lewis base type, 3) lattice-bound and 4) isolated hydroxy groups and anionic and cationic vacancies. An edge or even more so, a corner O²⁻ anion is coordinatively unsaturated and is seeking Lewis acids to help stabilize and delocalize its negative charge. Conversely, an Mg²⁺ ion on an edge or corner is seeking Lewis bases to stabilize and delocalize its positive charge. Therefore, these coordinatively unsaturated O²⁻ and Mg²⁺ ions readily accept incoming reagents with Lewis acid or Lewis base character.

The reaction proceeded moderately well with Pd-MgLaO, but with commercially available 10% Pd-C, it became extremely sluggish at room temperature. In the presence of Pd-SiO₂, the reaction did not form any perceptible amount of product.

Later, screening of various solvent systems using [NAP-Mg-Pd(0)] catalyst showed that THF is the most suitable solvent for this reaction (Table 2). Among the others, toluene and DMF gave the reaction product in moderate yields. Interestingly, the reaction did not proceed at all in methanol or isopropyl alcohol to give the desired product but resulted in the formation of some unidentified product. This phenomenon, though uncommon in the field of catalytic hydrogenation, may be attributed to the leaching of palladium from the support in alcoholic solvents.

It was found that the reaction works selectively and efficiently with a wide range of nitro-substituted aromatic compounds under atmospheric pressure and at room temperature (Table 3). During the reduction of 4-nitrohalobenzenes, such as 4-nitroiodobenzene and 4-nitrobromobenzene, trace amounts of the dehalogenated products were formed, although for 4-nitrochlorobenzene and 4-nitrofluorobenzene, no dehalo-



Scheme 2. Preparation of nanocrystalline MgO-stabilized palladium catalyst.

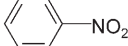
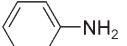
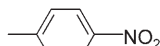
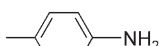
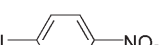
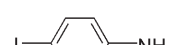
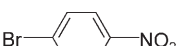
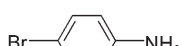
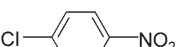
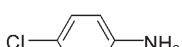
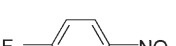
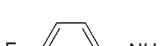


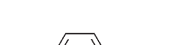




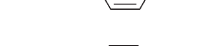


Table 2. Effect of various solvents for the reduction of nitrobenzene using [NAP-Mg-Pd(0)].^[a]

Entry	Solvent	Time [h]	Conversion [%] ^[b]
1	THF	2.0	98
2	toluene	2.0	85
3	DMF	2.0	60
4	methanol	2.0	-
5	isopropyl alcohol	2.0	-

^[a] Reaction conditions: nitrobenzene (1 mmol), NAP-Mg-Pd(0) (0.015 g), solvent (4 mL), room temperature, under H₂ atmosphere.

^[b] Determined by GC.

Table 3. Reduction of various nitroarenes using [NAP-Mg-Pd(0)].^[a]

Entry	Substrate	Product ^[b]	Time [h]	Yield [%] ^[c]
1			2.0	98, 98 ^[d] , 74 ^[e]
2			3.5	90
3			2.5	98
4			2.5	93
5			2.0	98
6			2.0	98
7			1.0	98
8			1.5	98
9			3.0	98
10			2.0	95
11			3.0	93

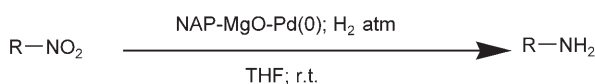
^[a] Reaction conditions: Aromatic nitro compound (1 mmol), NAP-Mg-Pd(0) (0.015 g, 1.48 mol%), dry THF (4 mL), room temperature, under H₂ atmosphere

^[b] All the products were characterized by comparison of their ¹H NMR spectra with those of the authentic samples.

^[c] NMR yields based on the nitroaromatics.

^[d] Yield after fifth cycle.

^[e] Yield after tenth cycle.



R = alkyl group



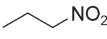
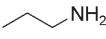


Scheme 3. Reduction of aliphatic nitro compounds.

generated products were detected. Even in the presence of electron-donating groups (Table 3, entries 2 and 8), the reaction proceeds under room temperature and atmospheric pressure to afford the product in almost quantitative yields. Chemoselective reduction was observed in the case of substrates like 4-nitrobenzaldehyde and 4-nitroacetophenone in which the carbonyl groups remained intact (Table 3, entries 9 and 10).

To widen the scope of the catalyst, several aliphatic nitro compounds were then subjected to reduction to their corresponding amines under the same reaction conditions (Scheme 3). These substrates also afforded the products in moderate to good yields (Table 4) although they required much longer reaction times than those of the aromatic nitro compounds.

The catalyst was recovered by simple filtration after the reaction and the filtrate was analyzed for leaching of palladium metal using AAS and it was observed that there was no leaching of palladium metal during the course of the reaction. NAP-Mg-Pd(0) catalyst was recovered and reused without further activation up to ten cycles (Table 3, entry 1). A slight decrease in the activity of the catalyst was found in the course of the recycling experiments. The small amount of decrease in the activity of the catalyst may be attributed to decrease in the surface area due to hydration of the catalyst by water formed in the reaction.^[4]

Table 4. Reduction of various aliphatic nitro compounds under H₂ atmosphere using [NAP-Mg-Pd(0)].^[a]

Entry	Substrate	Product ^[b]	Time [h]	Yield [%] ^[c]
1	—NO ₂	—NH ₂	4.5	92
2			6.5	88
3			6.5	88
4			4.5	92

^[a] Reaction conditions: Aliphatic nitro compound (1 mmol), NAP-MgO-Pd(0) (0.015 g, 1.48 mol%), dry THF (4 mL), room temperature, under H₂ atmosphere.

^[b] All the products were characterized by comparison of their ¹H NMR spectra with those of the authentic samples.

^[c] NMR yields based on the nitroaliphatic compound.

In order to know the influence of the reactants on the monodispersed [NAP-Mg-Pd(0)] particles, the used catalyst was analyzed by transmission electron microscopy (TEM) after the fifth cycle. The TEM image of the used catalyst did not show any change in the shape and size of the support as well as the active species, Pd(0). This suggests that the morphology of the catalyst remains the same even after several recycles (Figure 1a and b).

The X-ray powder diffraction (XRD) patterns of NAP-MgO, NAP-Mg-PdCl₄, fresh NAP-Mg-Pd(0) catalyst and used NAP-Mg-Pd(0) catalyst are shown in Figure 2. It shows that the surface of the NAP-MgO is hydroxylated to Mg(OH)_n during the preparative protocol (Scheme 2). On comparison, the patterns of the fresh and used catalyst Figure 2c and d remain the same in the range 2θ = 2°–80° which confirms that the structure and morphology of the catalyst remain the same during the course of the reaction.

In conclusion, the reduction of a wide range of organic nitro compounds to the corresponding amines in good to excellent yields has been achieved using a recyclable heterogeneous catalyst, [NAP-Mg-Pd(0)]. This method is mild, exceedingly efficient and highly selective. A wide range of functional groups is well tolerated under the reaction conditions. The method utilizes easy handling procedures, and the separation of the products from the reaction system can be achieved by simple filtration followed by solvent removal.

Experimental Section

Preparation of the Catalyst

The catalyst [NAP-Mg-Pd(0)] was prepared according to the procedure reported in the literature.^[14] Other catalysts were synthesized based on the literature reports.^[17,18]

Preparation of Nanocrystalline MgO Stabilized Palladium Catalyst

NAP-Mg-PdCl₄: NAP-MgO (BET 600 m² g⁻¹, 1 g) was treated with Na₂PdCl₄ (294 mg, 1 mmol) dissolved in 100 mL de-carbonated water with stirring for 12 h under a nitrogen atmosphere to afford the brown colored NAP-Mg-PdCl₄. Then the catalyst was filtered, and washed with deionized water, acetone, and dried.

NAP-Mg-Pd(0): NAP-Mg-PdCl₄ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in 20 mL dry ethanol for 3 h under a nitrogen atmosphere to get the black-colored, air-stable NAP-Mg-Pd(0) (Pd 0.99 mmol g⁻¹).

General Procedure for the Reduction of Nitro Compounds

The catalyst [NAP-Mg-Pd(0)] (0.015 g, 1.48 mol%) was suspended in dry THF (2 mL) and a hydrogen balloon was

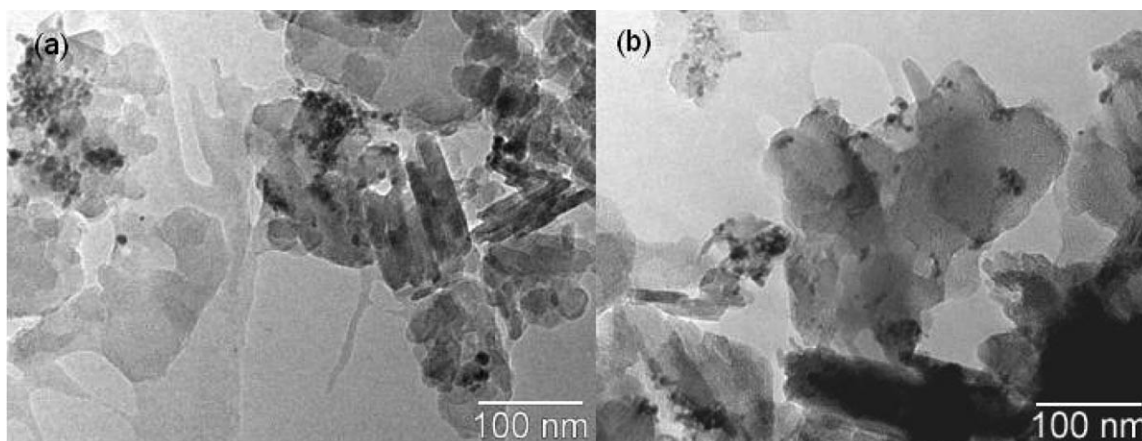


Figure 1. Transmission electron micrographs of [NAP-Mg-Pd(0)] (a) fresh (b) used.

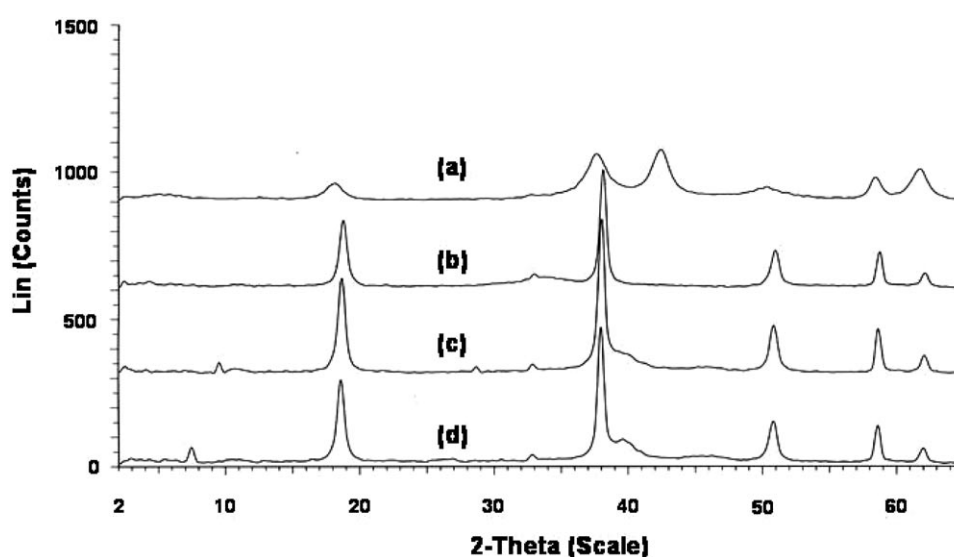


Figure 2. XRD patterns of (a) NAP-MgO, (b) NAP-Mg-PdCl₄, (c) NAP-Mg-Pd(0)-fresh catalyst, (d) NAP-Mg-Pd(0)-used catalyst.

fitted to the flask. The suspended catalyst was stirred under a hydrogen atmosphere for 20 min at room temperature and then a solution of the nitro compound (1 mmol) dissolved in dry THF (2 mL) was added to it. The resultant solution was stirred under hydrogen atmosphere at room temperature for the specified period. The progress of the reaction was monitored by TLC and GC. The reaction mixture was filtered and the solvent was removed under reduced pressure. The resulting products were analyzed by ¹H NMR and IR spectroscopic methods.

Reuse of the Catalyst

After completion of the reaction the catalyst was recovered by filtration and washed several times with ethyl acetate and then ether and dried under a nitrogen flow for further reuse. The catalyst showed consistent activity for ten cycles.

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