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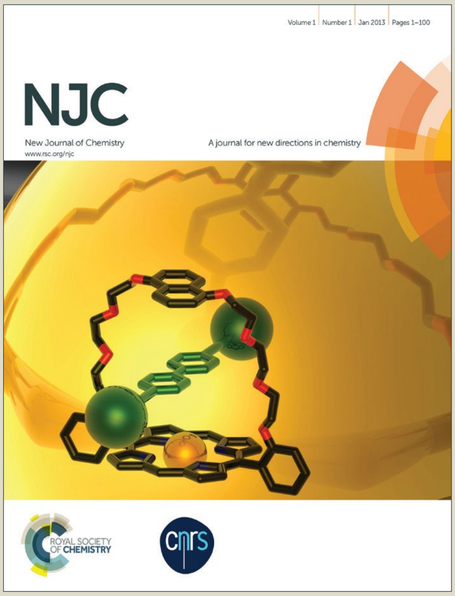

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Recyclable aluminium oxy-hydroxide supported Pd nanoparticles for selective hydrogenation of nitro compounds via sodium borohydride hydrolysis

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The reduction of aromatic/aliphatic nitro compounds to primary amines with high yields was easily realized by a transfer hydrogenation comprising commercially available aluminium oxy-hydroxide-supported Pd nanoparticles (0.5 wt% Pd, Pd/AlO(OH)) as catalysts and $NaBH_4$ as the hydrogen reservoir at room temperature in a water/methanol mixture (v/v = 7/3). The presented catalytic methodology is highly efficient for the reduction of various nitro compounds as well as being reusable. A variety of R-NO_2 derivatives were tested by undergoing the Pd/AlO(OH) catalysed reduction reaction and all the nitro compounds were selectively reduced into corresponding primary amines in reaction times ranging from 0.75 to 13 min with yields reaching up to 99%. This process can be assessed as an eco-friendly method with both reusable catalysts (Pd/AlO(OH) NPs) and hydrogen source ($NaBH_4$).

Introduction

Amino compounds are of great importance since they act as an intermediate for the synthesis of valuable organic molecules such as dyes, polymers, pesticides, antioxidants, drugs and agrochemicals.[1] Due to their enzyme inhibitory and antibiotic effects, they are an integral part of many important natural products.[2] For example, the commercially available drugs actinomycin and rifamycin respectively exhibit anticancer and antibacterial effects.[3] Recently, synthetic organic chemists have focused on the synthesis of naturally occurring and unnatural primary amines to study the relationship between structure and biological activity.[4] Amino compounds are generally formed by the reduction of imines[5] or nitriles,[6] hydroamination of olefines,[7] reductive amination of carbonyl compounds[8] and decarboxylation of carbamic acids.[9] Among the methods of synthesising amino compounds, hydrogenation of nitro compounds is quite common, effective and advantageous due to the formation of high-performance products.[10] Furthermore, hydrogenation of nitroarenes is the best way to achieve industrially important aryl amines.[11] However, the classical hydrogenation methods have several disadvantages such as the hazards presented by molecular hydrogen at high pressures and temperatures and the difficulties of isolating homogeneous catalysts and specialised equipment requirements.[12,13]

There are some materials used as both solvents and hydrogen sources in the transfer hydrogenation process. The use of ethanol,[14] isopropanol,[15] glycerol[16] and 1,4-cyclohexadiene[17] type solvents for the transfer hydrogenation method is widespread[18] because they are quite cheap, eco-friendly and safe.[19] However, dehydrogenation of those solvents requires high temperatures, high pressure, long reaction times and special equipments. In addition, the low yields of desired products are generally obtained. On the other hand, when used as solid hydrogen storage material, $NaBH_4$[20-22] is an effective hydrogen source compared to chemical hydrides such as $LiAlH_4$,[23] MgH_2,[23] and NH_3BH_3,[24] and acts as a liquid fuel after dissolution in water. It is non-toxic, non-flammable, easily accessible, highly stable, cost-effective and water-soluble as well as having high volume/mass hydrogen density (10.8 wt.%). Four moles of hydrogen gas per one mole $NaBH_4$ can easily be generated via its dehydrogenation in the presence of catalyst and water at room temperature.[25,26] The exothermic hydrolysis reaction of $NaBH_4$ is shown below:

$$NaBH_4 + 2H_2O \xrightarrow{\text{Catalyst}} NaBO_2 + 4H_2$$

Dehydrogenation of $NaBH_4$ can be carried out without a catalyst, but hydrogenation of unsaturated organic compounds cannot be achieved in such a way.[11,27] Noble metals such as Pt, Pd, Ru, Rh, Ir and transition metals such as Ni, Fe and Cu have frequently been used as homogeneous/heterogeneous catalysts for the reduction of nitro compounds.[16,28] Palladium-based heterogeneous catalysts in particular have greatly facilitated the hydrogenation of nitro compounds.[29] Our recent studies showed that NiPd NPs and CoPd NPs were highly efficient catalysts for

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† Electronic Supplementary Information (ESI) available: NMR spectra and spectral data of amine compounds and previous hydrogenation reactions. See DOI: 10.1039/x0xx00000x

reduction of nitro and/or nitrile compounds to primary amines with high yields.[24]

We report herein an economical and eco-friendly process for catalytic transfer reduction of various nitro compounds comprising Pd/AlO(OH) NPs (0.5 wt% Pd) as catalysts and $NaBH_4$ as hydrogen reservoir under mild conditions, without the use of H_2 gas pressure. Dehydrogenation of $NaBH_4$ in a water/methanol mixture (v/v = 7/3) and the subsequent hydrogenation of nitro compounds in the presence of Pd/AlO(OH) nanoparticles (NPs) were well established at room temperature. The catalytic activity of their substrates in the reduction reactions was identified. It was observed that various primer amines were successfully obtained, with isolated yields reaching up to 99% within reaction times ranging from 0.75 to 13 min (Table 3).

Results and discussion

In previous reports, commercially available aluminium oxy-hydroxide-supported Pd NPs (0.5 wt% of Pd, Pd/AlO(OH) NPs) have been used as catalysts for alkene hydrogenation and aerobic alcohol oxidation as well as for the dynamic kinetic resolution of primary amines.[30] This studies strongly indicates that Pd/AlO(OH) NPs have a number of advantages, such as being effective, recoverable and reusable. Furthermore, using such commercial catalysts is quite important for prevention of unnecessary chemical overuse. In this study, Pd/AlO(OH) NPs were used for first time in the selective reduction of nitro compounds as compared to nitrile compounds.

Fig. 1 shows representative scanning electronic microscopy (SEM) images of pristine Pd/AlO(OH) NPs (Fig. 1A) and Pd/AlO(OH) NPs after the consecutive ten runs catalytic reaction (Fig. 1B). As can be seen by the SEM images, there is no significant change on the morphology of Pd/AlO(OH) catalysts after the catalytic reaction, but an increase in the particle size could be concluded. Additionally, the elemental composition of the commercially available Pd/AlO(OH) catalysts and after the reaction was identified by EDX analysis (Figure 2A and 2B, respectively). The EDX spectra shows all the expected elements Pd, Al, O and C (for more information see ESI,† Fig. S1,2). Upon the comparison of EDX spectra of the commercially available catalysts and the catalysts after the reaction, it can be concluded that the initial elemental composition of the catalysts is preserved.

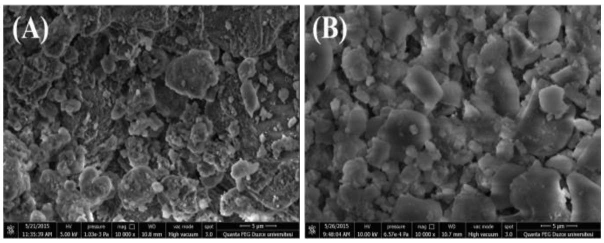


Fig. 1 (A) SEM image before the reaction; (B) SEM image after using ten times of Pd/AlO(OH) NPs.

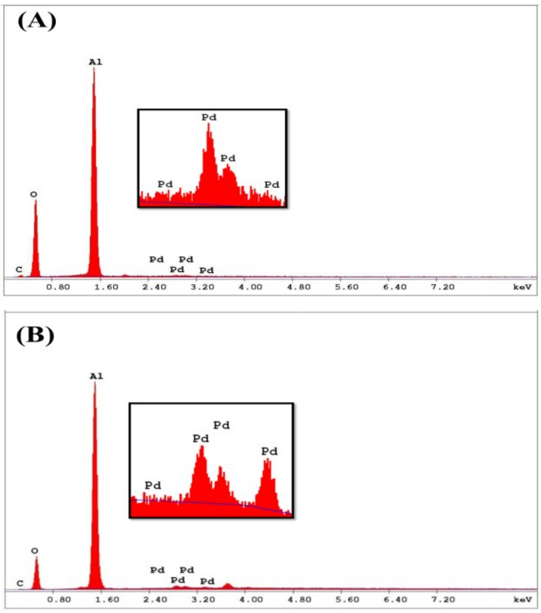


Fig. 2 (A) EDX spectrum before the reaction; (B) EDX spectrum after using ten times of Pd/AlO(OH) NPs.

Finally, X-ray diffraction pattern of the commercially available Pd/AlO(OH) catalyst was studied to elucidate its crystal structure (Fig. 3). There is no peak was appeared for Pd because commercially available Pd/AlO(OH) catalyst include only 0.5 wt% Pd metal. The other peaks can be easily attributed to the nanocrystalline Boehmite structure of aluminum oxide.[31]

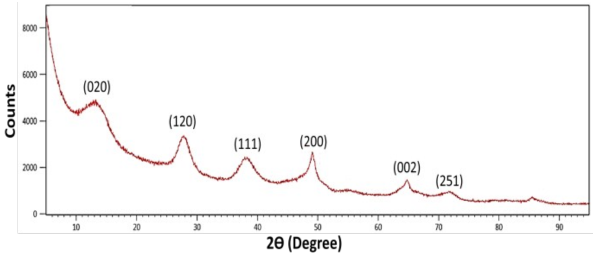
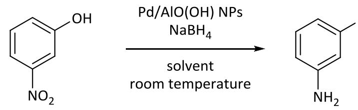


Fig. 3 XRD pattern spectrum of Pd/AlO(OH).

In this study, the effect of $NaBH_4$ (different $NaBH_4$/3-nitrophenol ratios), the effect of Pd/AlO(OH) NPs (different Pd/AlO(OH)/3-nitrophenol ratios) and the effect of the solvent (water, methanol, dichloromethane and water/methanol mixture) were examined. The yields were increased by increasing the amounts of $NaBH_4$ and Pd/AlO(OH) NPs. Before the main experiments, a controlled reaction was performed with 3 mmol of $NaBH_4$ and 25 mg of Pd/AlO(OH) NPs, with seemingly sufficient results. Because of the water-insoluble organic molecules, water/methanol mixture was used as solvent. Furthermore, the reduction reaction did not occur in the absence of catalyst. Optimization experiments showed optimum reaction conditions to

Table 1 Optimization of the conditions for reduction of 3-nitrophenol to 3-aminophenol[a]



Entry	Solvent	Catalyst (mg)	$NaBH_4$ (mmol)	Time (min)	Yield[b] (%)
1	H_2O	25	3	0.7	>99
2	MeOH	25	3	90	60
3	EtOH	25	3	300	No reaction
4	CH_2Cl_2	25	3	300	No reaction
5	**H_2O/MeOH (7:3)**	**25**	**3**	**1.15**	**>99**
6	H_2O/MeOH (7:3)	25	1	300	10
7	H_2O/MeOH (7:3)	25	2	3	>99
8	H_2O/MeOH (7:3)	25	4	1	>99
9	H_2O/MeOH (1:1)	25	3	1	>99
10	H_2O/MeOH (3:7)	25	3	5	>99
11	H_2O/MeOH (7:3)	5	3	20	>99
12	H_2O/MeOH (7:3)	10	3	9	>99
13	H_2O/MeOH (7:3)	15	3	5	>99
14	H_2O/MeOH (7:3)	20	3	3	>99
15	H_2O/MeOH (7:3)	100	3	0.5	>99
16	H_2O/MeOH (7:3)	-	3	300	No reaction

[a] Reaction conditions: 3-nitrophenol (1 mmol), Pd/AlO(OH) NPs (0.5 wt% Pd) and room temperature. [b] Isolated yield, determined by ^{1}H and ^{13}C NMR.

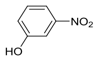
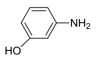
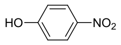
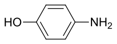
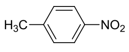
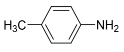
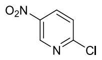
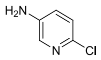
be 1 mmol of substrate, 3 mmol of $NaBH_4$, 25 mg of Pd/AlO(OH) NPs (0.5 wt% Pd), a water/methanol mixture (v/v = 7/3) and room temperature (Table 1).

The hydrogen release with the hydrolysis of $NaBH_4$ in water is a fast reaction. This situation may cause safety concerns and problems with quality when conducting the scale-up process. To control the hydrogen release, NaOH in the range 5-15 wt% is added gradually. The alkaline $NaBH_4$ solution decreases the catalyst efficiency. However, the excess amount of NaOH decreases the hydrogen yield.[25,27,32] Hydrolysis reaction of alkaline $NaBH_4$ solution is shown below:

$$BH_4^- + 4OH^- \xrightarrow{\text{Catalyst}} BO_2^- + 2H_2 + 2H_2O$$

Table 2 Pd/AlO(OH) NPs catalyzed reduction of various R-NO_2 compounds in alkaline $NaBH_4$ solution[a]

$$R\text{-}NO_2 \xrightarrow[\text{water/methanol (v/v:7/3), room temperature}]{\text{0.1 mmol\% Pd/AlO(OH) NPs, 3 eq. NaBH}_4\text{, NaOH (15 wt\%)}} R\text{-}NH_2$$

Entry	Substrate	Product	Yield[b] (%)	Time (min)
1			>99	14
2			>99	55
3			98	52
4			98	50

[a] Reaction conditions: substrate (1 mmol), $NaBH_4$ (3 mmol), Pd/AlO(OH) NPs (25 mg, 0.5 wt% Pd), NaOH (15 wt%), 1 ml of water/methanol (v/v = 7/3) and room temperature. [b] Isolated yield, determined by ^{1}H and ^{13}C NMR.

NaOH (15 wt%) was used in the reduction of some nitroarenes. Table 2 shows that the reduction of the corresponding nitroarenes seemed to be a slower process, with high yields in the alkaline $NaBH_4$ solution.

The sodium metaborate ($NaBO_2$) is obtained by the hydrolysis reaction of $NaBH_4$. It can be removed from the reaction medium by simple methods such as extraction, filtration etc. It is not seen as a problem to not interact with the starting material and product. Even if this waste material is reacted with hydrogen under appropriate conditions, it would be converted to $NaBH_4$.[33]

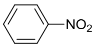
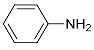
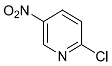
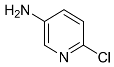
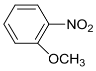
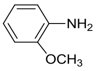
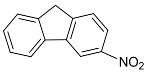
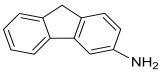
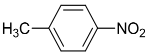
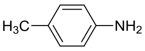
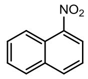
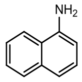
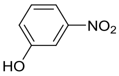
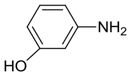
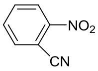
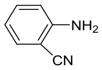
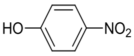
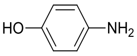
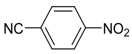
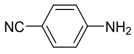
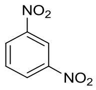
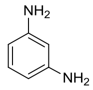
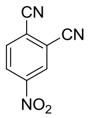
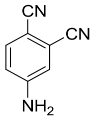
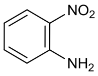
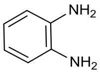
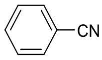
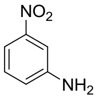
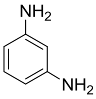
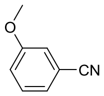
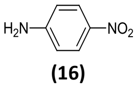
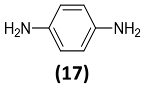
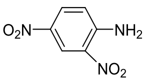
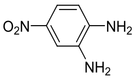
Table 3 summarises the results obtained from Pd/AlO(OH) catalysed reactions. In the series of aromatic and aliphatic nitro compounds tested, all of the compounds were reduced to the corresponding primary amines with excellent yields in 0.75-13 min at room temperature. Nitrobenzene (1) was quantitatively reduced to aniline (2) in 5 min (Table 3, entry 1). Electron-donating groups such as methoxy-, methyl- and hydroxyl-substituted nitrobenzenes (3, 5, 7, 9) were reduced to amines (4, 6, 8, 10) with quantitative yields (Table 3, entries 2-5). For 1,3-dinitrobenzene (11), both NO_2 groups were reduced quantitatively to NH_2 (12) after completion of the reaction within 4 min. (Table 3, entry 6). The 2-nitro aniline (13) and 4-nitro aniline (16) were reduced to corresponding NH_2 derivatives (14, 17) in a short time due to the electronic/conjugation effect (Table 3, entries 7, 9), whereas reduction of 3-nitro aniline (15) seemed to be a slower process with a quantitative yield. When the amount of Pd/AlO(OH) NPs were increased (50 mg), the reduction process became faster (Table 3, entry 8).

Surprisingly, the reduction of 2,4-dinitroaniline (18) was not achieved under the same conditions. However, 4-nitrobenzene-1,2-diamine (19) was formed by increasing the amount of hydrogen source (6 mmol of $NaBH_4$), where orto substituted nitro group was regioselectively reduced due to the electronic/conjugation effect (Table 3, entry 10). The Pd/AlO(OH) NPs provided a reduction of 2-chloro-5-nitropyridine (20), 3-nitro-9H-fluorene (22) and 2-nitro-naphthyl (24) compounds under mild conditions. They were all converted to their respective amine derivatives (21, 23, 25) with quantitative yields (Table 3, entries 11-13).

Electron-withdrawing groups such as –CN substituted nitro compounds were also tested for reduction process and selective reduction was observed.[24] While –NO_2 groups were exclusively reduced to amines, –CN groups were not dramatically affected (Table 3, entries 14-16). For instance, the reaction of 2-nitro benzonitrile (26) with $NaBH_4$ in the presence of Pd/AlO(OH) gave 2-amino benzonitrile (27) as the sole product, which indicated selective nitro group reduction (Table 3, entry 14). Benzonitrile (32)

Table 3 Pd/AlO(OH) NPs catalyzed reduction of various R-NO$_2$ compounds[a]

$$\text{R-NO}_2 \xrightarrow[\text{water/methanol (v/v:7/3), room temperature}]{\text{0.1 mmol\% Pd/AlO(OH) NPs, 3 eq. NaBH}_4} \text{R-NH}_2$$

Entry	Substrate	Product	Yield[d] (%)	Time (min)	Entry	Substrate	Product	Yield[d] (%)	Time (min)
1	 **(1)**	 **(2)**	>99	5	11	 **(20)**	 **(21)**	>99	5
2	 **(3)**	 **(4)**	>99	5	12	 **(22)**	 **(23)**	>99	9
3	 **(5)**	 **(6)**	>99	6	13	 **(24)**	 **(25)**	>99	6.45
4	 **(7)**	 **(8)**	>99	1.15	14	 **(26)**	 **(27)**	>99	4
5	 **(9)**	 **(10)**	>99	6	15	 **(28)**	 **(29)**	>99	13
6	 **(11)**	 **(12)**	>99	4	16	 **(30)**	 **(31)**	>99	0.75
7	 **(13)**	 **(14)**	>99	4.5	17	 **(32)**	-	No reaction	48 h
8	 **(15)**	 **(12)**	>99	3[b]	18	 **(33)**	-	No reaction	48 h
9	 **(16)**	 **(17)**	>99	6	19	CH_3NO_2 **(34)**	CH_3NH_2 **(35)**	>99	4
10	 **(18)**	 **(19)**	>99	7[c]	20	$CH_3CH_2NO_2$ **(36)**	$CH_3CH_2NH_2$ **(37)**	>99	4

[a] Unless otherwise stated, substrate (1 mmol), NaBH$_4$ (3 mmol) and Pd/AlO(OH) NPs (25 mg, 0.5 wt% Pd) was used with 1 ml of water/methanol (v/v=7/3) at room temperature except **8** and **10.** [b] 50 mg of Pd/AlO(OH) (0.5 wt% Pd) catalyst was used. [c] 6 mmol of NaBH$_4$ was used. [d] Isolated yield, determined by ^{1}H and ^{13}C NMR.

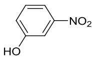
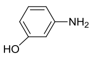
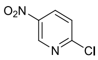
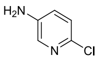
and 3-methoxybenzonitrile (33) were used as a substrate to prove the selective reduction. As a result, no reduction process was observed, despite the continuation of the reaction for 48 h (Table 3, entries 17, 18). This limited reduction was likely caused by the electronic/conjugation effect of –NH$_2$ on –CN, thus stabilizing the –CN against further reduction.

The transfer hydrogenation process was also accomplished for the aliphatic nitro compounds. Under mild conditions, methyl nitro (34) and ethyl nitro (36) compounds were easily converted to corresponding primary amines (35, 37) (Table 3, entries 19, 20).

It is recognized that recoverability and reusability are dominating factors for using heterogeneous catalysts.[10] The

Pd/AlO(OH) catalyst was subjected to a reusability test. It was observed that the catalyst preserved its efficiency when reused ten additional times (Table 4). The Pd content of commercial PdAlO(OH) catalyst is known to be 0.5 wt%. The ICP-OES analyses performed on the catalytic reaction solutions showed that a negligible amount of palladium was detected (<0.1 ppm, 0.8%). The value of the palladium leaching into the reaction solution after reuse is below 1% and thus can be tolerated. In this regard, the catalyst can be reused without decreasing the chemical yields of amino compounds.

Table 4 Reusing of Pd/AlO(OH) NPs[a]

Entry	Substrate	Product	1st run[b]	2nd run[b]	3rd run[b]	10th run[b]
1			>99	>99	>99	>99
2			>99	>99	>99	>99

[a] Reaction conditions: substrate (1 mmol), $NaBH_4$ (3 mmol), Pd/AlO(OH) NPs (25 mg, 0.5 wt% Pd), 1 ml of water/methanol (v/v = 7/3) and room temperature. [b] Isolated yield, determined by ^1H and ^{13}C NMR.

The PdAlO(OH) NPs and their catalytic activity can be suitably compared to other methods in the hydrogenation of 3-nitro phenol into 3-amino phenol (see ESI,† Table S1). As shown in the ESI,† Table S1, the different catalysts and reaction conditions affect the product yield and reaction time. The method developed in this study is better compared to some of the other methods (with a yield of <90%).[34] It is also an alternative method according to some (the yield being >99%).[24,35] For example, 3-nitro phenol converts into 3-amino phenol with the yield of 87% in 4 h in the presence of scrap automobile catalyst (SAC).[26] In another study, the Fe_3O_4@C@Pt catalyst ensures conversion of 3-nitro phenol into 3-amino phenol with the yield of 99% in 1h.[36] In general, other methods require longer time and a higher reaction temperature.

Many commercial catalysts are employed in hydrogenation studies. However, the use of PdAlO(OH) NPs in reduction reactions is quite recent. The activity of many commercial catalysts such as Pd/C decreases in an aqueous medium. In addition, these catalysts work more compatibly with hydrogen gas in an inert atmosphere (see ESI,† Table S2).[37] However, experimental results show that the activity of PdAlO(OH) NPs in water is quite good. Furthermore, the method developed in the presence of PdAlO(OH) NPs have several advantages such as a short reaction time and a low temperature requirement, unlike commercial catalysts. It does not involve the dangers posed by molecular hydrogen gas. Most importantly, PdAlO(OH) NPs are able to perform reduction reactions with hydrogen gas at room temperature and without a solvent.[30a]

The Pd/C catalyst was used for the reduction of 1-methyl-4-nitrobenzene to 1-methyl-4-aminobenzene under the same conditions developed in this study. Reduction of 5 was a slightly slower process, not reaching 100% conversion (chemical yield 68%) after 9 min of reaction (Table 5, entry 1). However, 5 was reduced to 6 with the yield higher than 99% within 6 min in the presence of PdAlO(OH) NPs (Table 3, entry 3). The NMR spectra obtained without any chromatographic processes provide clear evidence for the results (see ESI,† Fig. S3). The alkaline $NaBH_4$ solution used to control hydrogen release in the scale-up process carried out with the Pd/C catalyst impeded the reduction of nitro compounds (Table 5, entry 2).[38] Under the same conditions, PdAlO(OH) NPs extended the reaction time (52 min), but the product was formed with the yield of 98% (Table 2, entry 3). In the Table 5, the control experiments made with commercial catalysts such as Pd/C, Fe_3O_4, $Cu(Acac)_2$ and PdAlO(OH) showed that the present catalyst (PdAlO(OH)) gives the best result in the reduction of 1-methyl-4-nitrobenzene.

Table 5 The reduction of 1-methyl-4-nitrobenzene in the presence different commercial catalysts[a]

Entry	Catalyst (amount)	Yield[d] (%)	Time (min)
1	Pd/C (2.5 mg)	68	9[b]
2	Pd/C (2.5 mg)	25	30[c]
3	Fe_3O_4 (0.003 mmol)	42	10
4	$Cu(Acac)_2$ (0.003 mmol)	60	10
5	PdAlO(OH) (25 mg)	>99	6

[a] Reaction conditions: substrate (1 mmol), $NaBH_4$ (3 mmol), 1 ml of water/methanol (v/v = 7/3) and room temperature. [b] Catalyst (2.5 mg, 5 wt% Pd). [c] Catalyst (2.5 mg, 5 wt% Pd) and NaOH (15 wt%). [d] Isolated yield, determined by ^1H and ^{13}C NMR.

Additionally, the PdAlO(OH) NPs have a further important advantage due to the selective reduction of nitro groups compared to nitrile groups. Many commercially known catalysts such as Pd/C, Pt/C and Rh/C achieve the reduction of nitrile compounds to primary amines.[39] The reduction of benzonitrile to phenylmethanamine in the presence of Pd/C catalyst was observed in the given reaction conditions (see ESI,† Fig. S4).

Conclusions

In conclusion, an efficient catalyst system for the selective reduction of aromatic/aliphatic nitro compounds was well established. The reduction was carried out in an eco-friendly solvent mixture in which water, being an effective hydrogen donor of $NaBH_4$, was the main component. All substrates were successfully converted within 0.75-13 min to primary amines with excellent yields. The selective reduction of nitro groups compared to nitrile groups was also observed. Furthermore, the Pd/AlO(OH) catalyst was remained stable during the reduction process, even when used more than ten times. Hence, the many advantages of this reduction process include practicality, cost-effectiveness, safety, convenience and eco-friendliness.

Experimental

Materials

The synthesis was carried out using standard procedures and commercially available reagents. Pd/AlO(OH) NPs and all nitro and/or nitrile compounds used in the reduction reactions were purchased from Sigma-Aldrich. Chemicals were used without further purification.

Characterization methods

Before and after the reduction reaction, the surface analysis of the Pd/AlO(OH) catalyst was investigated by means of a scanning electron microscope (SEM: JEOL SEM5800) equipped with an energy dispersive X-ray (EDX) probe having an accelerator voltage of 20 keV. The X-ray diffraction (XRD) pattern was collected on a Rigaku diffractometer with a Cu Kα source operating at 40 kV and 40 mA generator. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer.

General procedure for the catalytic reduction of nitro compounds via $NaBH_4$ hydrolysis

The nitro and/or nitrile compounds (1 mmol), Pd/AlO(OH) catalyst (25 mg, 0.001 mmol Pd), and 1 ml of water/methanol (v/v=7/3) were stirred in a 100 ml sealed tube at room temperature. Next, $NaBH_4$ (3 mmol) was added to the reaction mixture. The reaction then continued while being vigorously stirred at room temperature. The progress of the catalytic reaction was monitored by thin-layered chromatography (TLC). Most of the reactions were completed over a time period of 0.75-13 min. The nitro groups were reduced, while the nitrile groups were not. After completion of the reaction, the Pd/AlO(OH) catalyst was recovered from the reaction media by simple centrifugation, washed with ethanol, dried under atmospheric conditions. The solvent was removed by using a rotary evaporator. Finally, the crude residue was directly purified by rapid column chromatography on silica gel using ethyl acetate/hexane. The yields of the reduced compounds were determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy using D_2O, DMSO, CD_3OD or $CDCl_3$ as the solvent, depending on the separated product.

Syntheses

Aniline (2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 9.0 Hz, 2H), 6.80 (t, *J* = 9.0 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 3.64 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 129.3, 118.5, 115.1.

2-Methoxy aniline (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.77 (m, 4H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 136.4, 121.2, 118.4, 115.1, 110.6, 55.5.

4-Aminotoluene (6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 8.3 Hz,2H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 129.7, 127.8, 115.7, 20.4.

3-Aminophenol (8). ^{1}H NMR (400 MHz, D_2O): δ 6.96 (m, 1H), 6.26 (m, 3H).

^{13}C NMR (100 MHz, D_2O): δ 130.8, 130.7, 130.6, 108.8, 106.6, 103.5.

4-Aminophenol (10). ^{1}H NMR (400 MHz, DMSO): δ 8.34 (s, 1H), 6.46 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (100 MHz, DMSO): δ 149.1, 140.9, 116.2, 116.1.

1,3-Diaminobenzene (12). ^{1}H NMR (400 MHz, D_2O): δ 6.91 (m, 1H), 6.17 (dd, *J* = 7.9, 2.0 Hz, 2H), 6.13 (s, 1H).

^{13}C NMR (100 MHz, D_2O): δ 147.2, 130.4, 130.3, 104.4.

1,2-Diaminobenzene (14). ^{1}H NMR (400 MHz, D_2O): δ 6.72-6.65 (m, 4H).

^{13}C NMR (100 MHz, D_2O): δ 134.2, 120.9, 117.8.

1,4-Diaminobenzene (17). ^{1}H NMR (400 MHz, D_2O): δ 6.62 (s, 4H), 4.64 (s, 4H).

^{13}C NMR (100 MHz, D_2O): δ 138.6, 118.1.

4-nitrobenzene-1,2-diamine (19). ^{1}H NMR (400 MHz, CD_3OD): δ 7.57 (m, 2H), 6.63 (m, 1H), 4.90 (s, 4H).

^{13}C NMR (100 MHz, CD_3OD): δ 142.3, 138.6, 137.1, 117.9, 113.5, 111.5.

2-Chloro-5-aminopyridine (21). ^{1}H NMR (400 MHz, D_2O): δ 7.74 (d, *J* = 2.9 Hz, 1H), 7.13 (br s, 2H).

^{13}C NMR (100 MHz, D_2O): δ 144.5, 136.5, 133.9, 126.0, 125.5.

2-Aminofluorene (23). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.71 (dd, *J* = 8.1, 2.2 Hz, 1H), 3.72 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 145.1, 142.3, 142.1, 132.9, 126.6, 125.1, 124.7, 120.6, 118.6, 113.9, 11.8, 36.8.

Naphthalen-1-amine (25). ^{1}H NMR (400MHz, CD_3OD): δ 7.95 (m, 1H), 7.73 (m, 1H), 7.39 (m, 2H), 7.22 (m, 2H), 6.80 (m, 1H).

^{13}C NMR (100MHz, CD_3OD): δ 143.3, 134.8, 128.0, 126.2, 125.4, 124.2, 121.4, 118.1, 109.5.

2-Aminobenzonitrile (27). ^{1}H NMR (400MHz, CD_3OD): δ 7.33–7.26 (m, 2H), 6.70 (m, 2H), 3.31 (br s, 2H).

^{13}C NMR (100MHz, CD_3OD): δ 151.5, 133.9, 132.1, 117.7, 116.4, 115.2.

4-Aminobenzonitrile (29). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 4.17 (br s, 2H).

^{13}C NMR (100MHz, $CDCl_3$): δ 150.4, 133.8, 120.1, 114.4, 100.1.

4-Aminophthalonitrile (31). ^{1}H NMR (400 MHz, DMSO): δ 7.61 (m, 1H), 6.99 (m, 1H), 6.85 (m, 1H).

^{13}C NMR (100 MHz, DMSO): δ 153.8, 135.7, 118.2, 117.9, 117.6.

Methanamine (35). ^{1}H NMR (400 MHz, D_2O): δ 2.55 (s, 3H).

^{13}C NMR (100MHz, D_2O): δ 38.2.

Ethanamine (37). ^{1}H NMR (400 MHz, D_2O): δ 2.84 (q, *J* = 6.9 Hz, 2H), 0.92 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100MHz, D_2O): δ 46.6, 9.2.

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Table of contents entry

Recyclable aluminium oxy-hydroxide supported Pd nanoparticles for selective hydrogenation of nitro compounds via sodium borohydride hydrolysis

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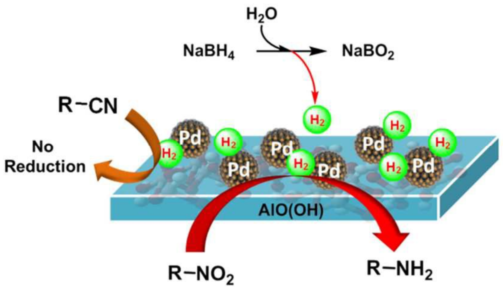

The method for the reduction of nitroarenes developed in the presence PdAlO(OH) NPs is simple, efficient and eco-friendly.