



Cite this: DOI: 10.1039/c5nj01492a

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

Haydar Göksu

The reduction of aromatic/aliphatic nitro compounds to primary amines with high yields was easily realized by transfer hydrogenation comprising commercially available aluminium oxy-hydroxide-supported Pd nanoparticles (0.5 wt% Pd, Pd/AlO(OH)) as catalysts and NaBH<sub>4</sub> 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 reusable. A variety of R-NO<sub>2</sub> derivatives were tested by performing the Pd/AlO(OH) catalysed reduction reaction and all the nitro compounds were selectively reduced to their 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 involving both reusable catalysts (Pd/AlO(OH) NPs) and hydrogen sources (NaBH<sub>4</sub>).

Received (in Montpellier, France)  
12th June 2015.

Accepted 18th August 2015

DOI: 10.1039/c5nj01492a

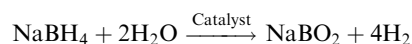
www.rsc.org/njc

## Introduction

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

pressures and temperatures and the difficulties in isolating homogeneous catalysts and specialised equipment requirements.<sup>12,13</sup>

There are some materials used as both solvents and hydrogen sources in the transfer hydrogenation process. The use of ethanol,<sup>14</sup> isopropanol,<sup>15</sup> glycerol<sup>16</sup> and 1,4-cyclohexadiene<sup>17</sup> type solvents for the transfer hydrogenation method is widespread<sup>18</sup> because they are quite cheap, eco-friendly and safe.<sup>19</sup> However, dehydrogenation of those solvents requires high temperatures, high pressures, long reaction times and special equipment. In addition, low yields of the desired products are generally obtained. On the other hand, when used as a solid hydrogen storage material, NaBH<sub>4</sub><sup>20–22</sup> is an effective hydrogen source compared to chemical hydrides such as LiAlH<sub>4</sub>,<sup>23</sup> MgH<sub>2</sub>,<sup>23</sup> and NH<sub>3</sub>BH<sub>3</sub>,<sup>24</sup> and acts as liquid fuel after dissolution in water. It is non-toxic, non-flammable, easily accessible, highly stable, cost-effective and water-soluble as well as has high volume/mass hydrogen density (10.8 wt%). Four moles of hydrogen gas per one mole of NaBH<sub>4</sub> can easily be generated *via* its dehydrogenation in the presence of a catalyst and water at room temperature.<sup>25,26</sup> The exothermic hydrolysis reaction of NaBH<sub>4</sub> is shown below:



Dehydrogenation of NaBH<sub>4</sub> can be carried out without a catalyst, but hydrogenation of unsaturated organic compounds cannot be achieved in such a way.<sup>11,27</sup> Noble metals such as Pt, Pd, Ru, Rh, and Ir and transition metals such as Ni, Fe and Cu have frequently been used as homogeneous/heterogeneous

Kaynasli Vocational College, Düzce University, Düzce 81900, Turkey.

E-mail: haydargoksu@duzce.edu.tr; Fax: +90 380 5442812; Tel: +90 380 5442811

† Electronic supplementary information (ESI) available: NMR spectra and spectral data of amine compounds and previous hydrogenation reactions. See DOI: 10.1039/c5nj01492a

catalysts for the reduction of nitro compounds.<sup>16,28</sup> Palladium-based heterogeneous catalysts in particular have greatly facilitated the hydrogenation of nitro compounds.<sup>29</sup> Our recent studies showed that NiPd NPs and CoPd NPs were highly efficient catalysts for the reduction of nitro and/or nitrile compounds to primary amines with high yields.<sup>24</sup>

We report herein an economical and eco-friendly process for the catalytic transfer reduction of various nitro compounds with Pd/AlO(OH) NPs (0.5 wt% Pd) as catalysts and NaBH<sub>4</sub> as a hydrogen reservoir under mild conditions, without the use of H<sub>2</sub> gas pressure. Dehydrogenation of NaBH<sub>4</sub> 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 oxyhydroxide-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.<sup>30</sup> These studies strongly indicate 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 the prevention of unnecessary chemical overuse. In this study, Pd/AlO(OH) NPs were used for the first time in the selective reduction of nitro compounds as compared to nitrile compounds.

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

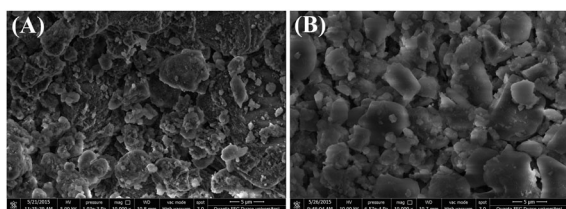


Fig. 1 (A) SEM image before the reaction; (B) SEM image after using ten times of Pd/AlO(OH) NPs.

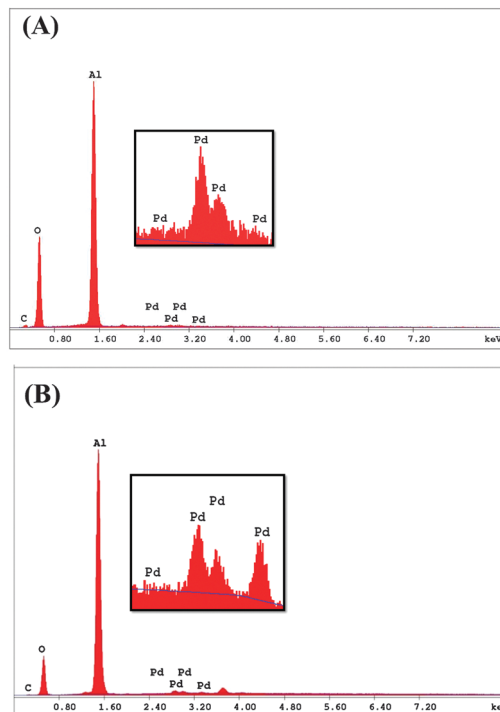


Fig. 2 (A) EDX spectrum before the reaction; (B) EDX spectrum after using ten times of Pd/AlO(OH) NPs.

be concluded that the initial elemental composition of the catalysts is preserved.

Finally, the X-ray diffraction pattern of the commercially available Pd/AlO(OH) catalyst was studied for the elucidation of its crystal structure (Fig. 3). No peak was observed for Pd because commercially available Pd/AlO(OH) catalysts include only 0.5 wt% of Pd metal. The other peaks can be easily attributed to the nanocrystalline Boehmite structure of aluminum oxide.<sup>31</sup>

In this study, the effect of NaBH<sub>4</sub> (different NaBH<sub>4</sub>/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<sub>4</sub> and Pd/AlO(OH) NPs. Before the main experiments, a controlled reaction was performed with 3 mmol of NaBH<sub>4</sub> and 25 mg of Pd/AlO(OH) NPs, with seemingly sufficient results. Because of the water-insoluble organic molecules, a water/methanol mixture was used as solvent. Furthermore, the reduction reaction did not occur in the absence of a catalyst.

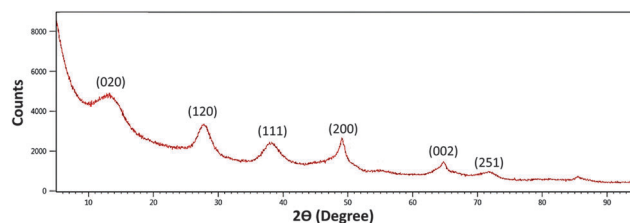
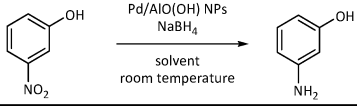


Fig. 3 XRD pattern of Pd/AlO(OH).

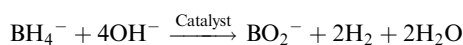
**Table 1** Optimization of the conditions for the reduction of 3-nitrophenol to 3-aminophenol<sup>a</sup>


Entry	Solvent	Catalyst (mg)	NaBH <sub>4</sub> (mmol)	Time (min)	Yield <sup>b</sup> (%)
1	H <sub>2</sub> O	25	3	0.7	> 99
2	MeOH	25	3	90	60
3	EtOH	25	3	300	No reaction
4	CH <sub>2</sub> Cl <sub>2</sub>	25	3	300	No reaction
5	H <sub>2</sub> O/MeOH (7 : 3)	25	3	1.15	> 99
6	H <sub>2</sub> O/MeOH (7 : 3)	25	1	300	10
7	H <sub>2</sub> O/MeOH (7 : 3)	25	2	3	> 99
8	H <sub>2</sub> O/MeOH (7 : 3)	25	4	1	> 99
9	H <sub>2</sub> O/MeOH (1 : 1)	25	3	1	> 99
10	H <sub>2</sub> O/MeOH (3 : 7)	25	3	5	> 99
11	H <sub>2</sub> O/MeOH (7 : 3)	5	3	20	> 99
12	H <sub>2</sub> O/MeOH (7 : 3)	10	3	9	> 99
13	H <sub>2</sub> O/MeOH (7 : 3)	15	3	5	> 99
14	H <sub>2</sub> O/MeOH (7 : 3)	20	3	3	> 99
15	H <sub>2</sub> O/MeOH (7 : 3)	100	3	0.5	> 99
16	H <sub>2</sub> O/MeOH (7 : 3)	—	3	300	No reaction

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

Optimization experiments showed the optimum reaction conditions to be 1 mmol of substrate, 3 mmol of NaBH<sub>4</sub>, 25 mg of Pd/AlO(OH) NPs (0.5 wt% Pd), a water/methanol mixture (v/v = 7/3) and room temperature (Table 1).

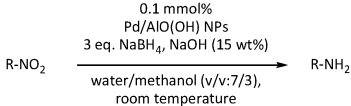
Hydrogen release with the hydrolysis of NaBH<sub>4</sub> in water is a fast reaction. This situation may raise safety concerns and problems with quality when conducting the scale-up process. To control the hydrogen release, NaOH in the range of 5–15 wt% is added gradually. The alkaline NaBH<sub>4</sub> solution decreases the catalyst efficiency. However, an excess amount of NaOH decreases the hydrogen yield.<sup>25,27,32</sup> Hydrolysis reaction of alkaline NaBH<sub>4</sub> solution is shown below:



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<sub>4</sub> solution.

Sodium metaborate (NaBO<sub>2</sub>) is obtained by the hydrolysis reaction of NaBH<sub>4</sub>. It can be removed from the reaction medium by simple methods such as extraction and filtration. It is not seen as a problem to not interact with the starting material and the product. Even if this waste material is reacted with hydrogen under appropriate conditions, it would be converted to NaBH<sub>4</sub>.<sup>33</sup>

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

**Table 2** Pd/AlO(OH) NP catalyzed reduction of various R-NO<sub>2</sub> compounds in alkaline NaBH<sub>4</sub> solution<sup>a</sup>


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

<sup>a</sup> Reaction conditions: substrate (1 mmol), NaBH<sub>4</sub> (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. <sup>b</sup> Isolated yield, determined by <sup>1</sup>H and <sup>13</sup>C NMR.







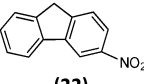
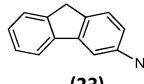
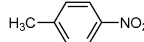







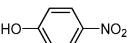
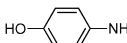
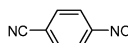












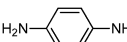
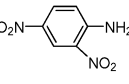
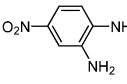
such as methoxy-, methyl- and hydroxyl-substituted nitrobenzenes (3, 5, 7, 9) were reduced to amines (4, 6, 8, 10) with quantitative yields (Table 3, entries 2–5). For 1,3-dinitrobenzene (11), both NO<sub>2</sub> groups were reduced quantitatively to NH<sub>2</sub> (12) after completion of the reaction within 4 min (Table 3, entry 6). The 2-nitro aniline (13) and 4-nitro aniline (16) were reduced to the corresponding NH<sub>2</sub> derivatives (14, 17) in a short time due to the electronic/conjugation effect (Table 3, entries 7 and 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 was 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<sub>4</sub>), where the *ortho* substituted nitro group was regioselectively reduced due to the electronic/conjugation effect (Table 3, entry 10). Pd/AlO(OH) NPs catalyzed the 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 the reduction process and selective reduction was observed.<sup>24</sup> While –NO<sub>2</sub> 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<sub>4</sub> 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) and 3-methoxybenzonitrile (33) were used as substrates to promote selective reduction. As a result, no reduction process was observed, despite the continuation of the reaction for 48 h (Table 3, entries 17 and 18). This limited reduction was likely caused by the electronic/conjugation effect of –NH<sub>2</sub> on –CN, thus stabilizing the –CN against further reduction.

The transfer hydrogenation process was also accomplished for the aliphatic nitro compounds. Under mild conditions,

Table 3 Pd/AIO(OH) NP catalyzed reduction of various R-NO<sub>2</sub> compounds<sup>a</sup>

		0.1 mmol% Pd/AIO(OH) NPs 3 eq. NaBH <sub>4</sub>				R-NH <sub>2</sub>			
		R-NO <sub>2</sub>		water/methanol (v/v:7/3), room temperature					
Entry	Substrate	Product	Yield <sup>d</sup> (%)	Time (min)	Entry	Substrate	Product	Yield <sup>d</sup> (%)	Time (min)
1			> 99	5	11			> 99	5
2			> 99	5	12			> 99	9
3			> 99	6	13			> 99	6.45
4			> 99	1.15	14			> 99	4
5			> 99	6	15			> 99	13
6			> 99	4	16			> 99	0.75
7			> 99	4.5	17		—	No reaction	48 h
8			> 99	3 <sup>b</sup>	18		—	No reaction	48 h
9			> 99	6	19	CH <sub>3</sub> NO <sub>2</sub> (34)	CH <sub>3</sub> NH <sub>2</sub> (35)	> 99	4
10			> 99	7 <sup>c</sup>	20	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub> (36)	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> (37)	> 99	4

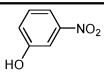
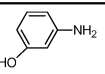
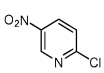
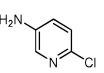
<sup>a</sup> Unless otherwise stated, substrate (1 mmol), NaBH<sub>4</sub> (3 mmol) and Pd/AIO(OH) NPs (25 mg, 0.5 wt% Pd) were used with 1 ml of water/methanol (v/v = 7/3) at room temperature except 8 and 10. <sup>b</sup> 50 mg of Pd/AIO(OH) (0.5 wt% Pd) catalyst was used. <sup>c</sup> 6 mmol of NaBH<sub>4</sub> was used. <sup>d</sup> Isolated yield, determined by <sup>1</sup>H and <sup>13</sup>C NMR.

methyl nitro (34) and ethyl nitro (36) compounds were easily converted to their corresponding primary amines (35 and 37) (Table 3, entries 19 and 20).

It is recognized that recoverability and reusability are dominating factors for using heterogeneous catalysts.<sup>10</sup> The Pd/AIO(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 the commercial Pd/AIO(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

Table 4 Reusing of Pd/AlO(OH) NPs<sup>a</sup>

Entry	Substrate	Product	1st run <sup>b</sup>	2nd run <sup>b</sup>	3rd run <sup>b</sup>	10th run <sup>b</sup>
1			> 99	> 99	> 99	> 99
2			> 99	> 99	> 99	> 99

<sup>a</sup> Reaction conditions: substrate (1 mmol), NaBH<sub>4</sub> (3 mmol), Pd/AlO(OH) NPs (25 mg, 0.5 wt% Pd), 1 ml of water/methanol (v/v = 7/3) and room temperature. <sup>b</sup> Isolated yield, determined by <sup>1</sup>H and <sup>13</sup>C NMR.

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.

PdAlO(OH) NPs and their catalytic activity can be suitably compared to other methods for the hydrogenation of 3-nitrophenol 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%).<sup>34</sup> It is also an alternative method according to some (the yield being >99%).<sup>24,35</sup> For example, 3-nitrophenol converts into 3-amino phenol with the yield of 87% in 4 h in the presence of a scrap automobile catalyst (SAC).<sup>26</sup> In another study, the Fe<sub>3</sub>O<sub>4</sub>@C@Pt catalyst ensures the conversion of 3-nitrophenol into 3-amino phenol with the yield of 99% in 1 h.<sup>36</sup> 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).<sup>37</sup> 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 has 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.<sup>30a</sup>

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<sub>4</sub> 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).<sup>38</sup> Under the same conditions, PdAlO(OH) NPs extended the reaction time (52 min), but the

Table 5 The reduction of 1-methyl-4-nitrobenzene in the presence of different commercial catalysts<sup>a</sup>

Entry	Catalyst (amount)	Yield <sup>d</sup> (%)	Time (min)
1	Pd/C (2.5 mg)	68	9 <sup>b</sup>
2	Pd/C (2.5 mg)	25	30 <sup>c</sup>
3	Fe <sub>3</sub> O <sub>4</sub> (0.003 mmol)	42	10
4	Cu(Acac) <sub>2</sub> (0.003 mmol)	60	10
5	PdAlO(OH) (25 mg)	> 99	6

<sup>a</sup> Reaction conditions: substrate (1 mmol), NaBH<sub>4</sub> (3 mmol), 1 ml of water/methanol (v/v = 7/3) and room temperature. <sup>b</sup> Catalyst (2.5 mg, 5 wt% Pd). <sup>c</sup> Catalyst (2.5 mg, 5 wt% Pd) and NaOH (15 wt%). <sup>d</sup> Isolated yield, determined by <sup>1</sup>H and <sup>13</sup>C NMR.

product was formed with the yield of 98% (Table 2, entry 3). In Table 5, the control experiments made with commercial catalysts such as Pd/C, Fe<sub>3</sub>O<sub>4</sub>, Cu(Acac)<sub>2</sub> and PdAlO(OH) showed that the present catalyst (PdAlO(OH)) gives the best result in the reduction of 1-methyl-4-nitrobenzene.

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.<sup>39</sup> The reduction of benzonitrile to phenylmethanamine in the presence of a Pd/C catalyst was observed under 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<sub>4</sub>, 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 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 K $\alpha$  source operating at 40 kV and 40 mA. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer.

### General procedure for the catalytic reduction of nitro compounds via $\text{NaBH}_4$ 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,  $\text{NaBH}_4$  (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 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  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy using  $\text{D}_2\text{O}$ , DMSO,  $\text{CD}_3\text{OD}$  or  $\text{CDCl}_3$  as the solvent, depending on the separated product.

### Syntheses

**Aniline (2).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.3, 129.3, 118.5, 115.1.

**2-Methoxy aniline (4).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.90–6.77 (m, 4H), 3.90 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.4, 136.4, 121.2, 118.4, 115.1, 110.6, 55.5.

**4-Aminotoluene (6).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (d,  $J = 7.9$  Hz, 2H), 6.65 (d,  $J = 8.3$  Hz, 2H), 2.24 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.9, 129.7, 127.8, 115.7, 20.4.

**3-Aminophenol (8).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  6.96 (m, 1H), 6.26 (m, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  130.8, 130.7, 130.6, 108.8, 106.6, 103.5.

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

$^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  149.1, 140.9, 116.2, 116.1.

**1,3-Diaminobenzene (12).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  6.91 (m, 1H), 6.17 (dd,  $J = 7.9, 2.0$  Hz, 2H), 6.13 (s, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  147.2, 130.4, 130.3, 104.4.

**1,2-Diaminobenzene (14).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  6.72–6.65 (m, 4H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  134.2, 120.9, 117.8.

**1,4-Diaminobenzene (17).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  6.62 (s, 4H), 4.64 (s, 4H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  138.6, 118.1.

**4-Nitrobenzene-1,2-diamine (19).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.57 (m, 2H), 6.63 (m, 1H), 4.90 (s, 4H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  142.3, 138.6, 137.1, 117.9, 113.5, 111.5.

**2-Chloro-5-aminopyridine (21).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.74 (d,  $J = 2.9$  Hz, 1H), 7.13 (br s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.5, 136.5, 133.9, 126.0, 125.5.

**2-Aminofluorene (23).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.95 (m, 1H), 7.73 (m, 1H), 7.39 (m, 2H), 7.22 (m, 2H), 6.80 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  143.3, 134.8, 128.0, 126.2, 125.4, 124.2, 121.4, 118.1, 109.5.

**2-Aminobenzonitrile (27).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.33–7.26 (m, 2H), 6.70 (m, 2H), 3.31 (br s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  151.5, 133.9, 132.1, 117.7, 116.4, 115.2.

**4-Aminobenzonitrile (29).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J = 8.6$  Hz, 2H), 6.63 (d,  $J = 8.6$  Hz, 2H), 4.17 (br s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.4, 133.8, 120.1, 114.4, 100.1.

**4-Aminophthalonitrile (31).**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  7.61 (m, 1H), 6.99 (m, 1H), 6.85 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  153.8, 135.7, 118.2, 117.9, 117.6.

**Methanamine (35).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.55 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  38.2.

**Ethanamine (37).**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.84 (q,  $J = 6.9$  Hz, 2H), 0.92 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  46.6, 9.2.

## Acknowledgements

The author is indebted to Kaynasli Vocational College at Düzce University and TUBA (Turkish Academy of Sciences) for their support of this work.

## Notes and references

- 1 A. F. Trasarti, N. M. Bertero, C. R. Apestequia and A. J. Marchi, *Appl. Catal., A*, 2014, **475**, 282–291.
- 2 D.-Z. Xu, H. Li and Y. Wang, *Tetrahedron*, 2012, **68**, 7867–7872.
- 3 K. W. Wellington and N. I. Kolesnikova, *Bioorg. Med. Chem.*, 2012, **20**, 4472–4481.
- 4 B. Wu, X. Gao, M.-W. Chen and Y.-G. Zhou, *Tetrahedron Lett.*, 2015, **56**, 1135–1137.
- 5 J. R. Miecznikowski and R. H. Crabtree, *Polyhedron*, 2004, **23**, 2857–2872.
- 6 I. Cabrita and A. C. Fernandes, *Tetrahedron*, 2011, **67**, 8183–8186.

- 7 C. A. Tsipis and C. E. Kefalidis, *Organometallics*, 2006, **25**, 1696–1706.
- 8 S. Ogo, K. Uehara, T. Abura and S. Fukuzumi, *J. Am. Chem. Soc.*, 2004, **126**, 3020–3021.
- 9 B. Ma and W. C. Lee, *Tetrahedron Lett.*, 2010, **51**, 385–386.
- 10 S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram and P. Selvam, *Tetrahedron Lett.*, 2002, **43**, 8527–8529.
- 11 (a) A. K. Shil, D. Sharma, N. R. Guha and P. Das, *Tetrahedron Lett.*, 2012, **53**, 4858–4861; (b) M. B. Gawande, H. Guo, A. K. Rathi, P. S. Branco, Y. Chen, R. S. Varma and D. L. Peng, *RSC Adv.*, 2013, **3**, 1050–1054.
- 12 A. Corma, C. Gonzalez-Arellano, M. Iglesias and F. Sanchez, *Appl. Catal., A*, 2009, **356**, 99–102.
- 13 M. M. Mdleleni, R. G. Rinker and P. C. Ford, *J. Mol. Catal. A: Chem.*, 2003, **204**, 125–131.
- 14 S. Chandrappa, K. Vinaya, T. Ramakrishnappa and K. S. Rangappa, *Synlett*, 2010, 3019–3022.
- 15 (a) S. U. Sonavane, M. B. Gawande, S. S. Deshpande, A. Venkataraman and R. V. Jayaram, *Catal. Commun.*, 2007, **8**, 1803–1806; (b) S. Farhadi and F. Siadatnasab, *J. Mol. Catal. A: Chem.*, 2011, **339**, 108–116.
- 16 (a) A. Wolfson, C. Dlugy, Y. Shotland and D. Tavor, *Tetrahedron Lett.*, 2009, **50**, 5951–5953; (b) Y. Gu and F. Jerome, *Green Chem.*, 2010, **12**, 1127–1138; (c) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski and O. M. N. D. Teodoro, *Chem. – Eur. J.*, 2012, **18**, 12628–12632; (d) M. B. Gawande, P. S. Branco, I. D. Nogueira, C. A. A. Ghumman, N. Bundaleski, A. Santos, O. M. N. D. Teodoro and R. Luque, *Green Chem.*, 2013, **15**, 682–689.
- 17 J. F. Quinn, C. E. Bryant, K. C. Golden and B. T. Gregg, *Tetrahedron Lett.*, 2010, **51**, 786–789.
- 18 (a) J. E. Backvall, *J. Organomet. Chem.*, 2002, **652**, 105–111; (b) D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621–6686.
- 19 G. Szollosi and M. Bartok, *Catal. Lett.*, 1999, **59**, 179–185.
- 20 Q. Li and H. Kim, *Fuel Process. Technol.*, 2012, **100**, 43–48.
- 21 G. Wang, X. Wang, R. Miao, D. Cao and K. Sun, *Int. J. Hydrogen Energy*, 2010, **35**, 1227–1231.
- 22 O. V. Netskina, A. M. Ozerova, O. V. Komova, G. V. Odegova and V. I. Simagina, *Catal. Today*, 2015, **245**, 86–92.
- 23 Y. Zhang, Q. F. Tian, S. S. Liu and L. X. Sun, *J. Power Sources*, 2008, **185**, 1514–1518.
- 24 (a) H. Goksu, H. Can, K. Sendil, M. S. Gultekin and O. Metin, *Appl. Catal., A*, 2014, **488**, 176–182; (b) H. Goksu, S. F. Ho, O. Metin, K. Korkmaz, A. M. Garcia, M. S. Gultekin and S. Sun, *ACS Catal.*, 2014, **4**, 1777–1782.
- 25 (a) N. Sahiner and A. O. Yasar, *Int. J. Hydrogen Energy*, 2014, **39**, 10476–10484; (b) N. Sahiner and A. O. Yasar, *Fuel Process. Technol.*, 2014, **125**, 148–154; (c) F. Seven and N. J. Sahiner, *J. Power Sources*, 2014, **272**, 128–136.
- 26 H. Genc, *Catal. Commun.*, 2015, **67**, 64–67.
- 27 M. H. Loghmani and A. F. Shojaei, *Energy*, 2014, **68**, 152–159.
- 28 F. A. Harraz, S. E. El-Hout, H. M. Killa and L. A. Ibrahim, *J. Catal.*, 2012, **286**, 184–192.
- 29 M. Shah, Q. X. Guo and Y. Fu, *Catal. Commun.*, 2015, **65**, 85–90.
- 30 (a) F. Chang, H. Kim, B. Lee, S. Park and J. Park, *Tetrahedron Lett.*, 2010, **51**, 4250–4252; (b) M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang and J. Park, *Org. Lett.*, 2005, **7**, 1077–1079; (c) M. J. Kim, W. H. Kim, K. Han, Y. K. Choi and J. Park, *Org. Lett.*, 2007, **9**, 1157–1159.
- 31 H. Hou, Y. Zhu and Q. Hu, *Mater. Trans., JIM*, 2013, **54**, 1686–1690.
- 32 (a) J. C. Ingersoll, N. Mani, T. C. Thenmozhiyal and A. Muthaiah, *J. Power Sources*, 2007, **173**, 450–457; (b) W. Wang, Y. Zhao, D. Chen, X. Wang, X. Peng and J. Tian, *Int. J. Hydrogen Energy*, 2014, **39**, 16202–16211.
- 33 (a) Y. Kojima and T. Haga, *Int. J. Hydrogen Energy*, 2003, **28**, 989–993; (b) C. Cakanyildirim and M. Guru, *Int. J. Hydrogen Energy*, 2008, **33**, 4634–4639.
- 34 (a) Y.-S. Feng, J.-J. Ma, Y.-M. Kang and H.-J. Xu, *Tetrahedron*, 2014, **70**, 6100–6105; (b) N. Salam, B. Banerjee, A. S. Roy, P. Mondal, S. Roy, A. Bhaumik and S. M. Islam, *Appl. Catal., A*, 2014, **477**, 184–194.
- 35 L. Huang, P. Luo, M. Xiong, R. Chen, Y. Wang, W. Xing and J. Huang, *Chin. J. Chem.*, 2013, **31**, 987–991.
- 36 M. Xie, F. Zhang, Y. Long and J. Ma, *RSC Adv.*, 2013, **3**, 10329–10334.
- 37 (a) J. W. Bae, Y. J. Cho, S. H. Lee and C. M. Yoon, *Tetrahedron Lett.*, 2000, **41**, 175–177; (b) J. Li, X.-Y. Shi, Y.-Y. Bi, J.-F. Wei and Z.-G. Chen, *ACS Catal.*, 2011, **1**, 657–664.
- 38 M. Lim, C. M. Yoon, G. An and H. Rhee, *Tetrahedron Lett.*, 2007, **48**, 3835–3839.
- 39 S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-Interscience, New York, 2001.