An efficient method for reduction of nitroaromatic compounds to the corresponding aromatic amines with $NH_2NH_2{\cdot}H_2O$ catalysed by H_2O_2-treated activated carbon

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An efficient and green protocol for the reduction of nitroaromatic compounds to the corresponding amines has been developed. The reduction catalyst system includes $NH_2NH_2{\cdot}H_2O$ and H_2O_2-treated activated carbon. Without adding additional metals, the H_2O_2-treated activated carbon could be reused for many cycles without decreasing catalytic efficiency. The aromatic amines could be obtained in good to excellent yields.

Keywords: nitro reduction, H_2O_2-treated activated carbon, hydrazine hydrate, aromatic amines

The reduction of nitroaromatic compounds is one of the most important chemical conversions for preparing the corresponding aromatic amines, which are important starting materials and intermediates for the manufacture of a great variety of chemicals.[1] Up to now, many reducing agents or systems used for the reduction of nitroaromatic compounds have been studied, such as hydrogen in the presence of metal (*e.g.* Fe), sodium sulfide, CO/H_2O, hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$) in the presence of metal ions and other methods.[2–15] Among the reducing systems, $NH_2NH_2{\cdot}H_2O$ has been paid great attention. The first example using $NH_2NH_2{\cdot}H_2O$ as a catalyst for the reduction of nitro compounds was reported by Busch and Schulz in 1929.[16] In the following years, a wide range of catalysts such as Pd/C, Cu, Fe, Ni, Rh/C, Ru/Ca, Raney nickel and Mo have been used in the reduction of aromatic nitro compounds to aromatic amines with $NH_2NH_2{\cdot}H_2O$ as hydrogen donor.[17–23] Furthermore, $NH_2NH_2{\cdot}H_2O$ has also been used alone for reducing nitroaromatic compounds in the absence of metals when the reaction conditions are very harsh.[24]

Activated carbon (AC) is usually used as a substrate for loading active catalytic centres due to its large surface area, tunable porosity and high stability in caustic and acidic conditions.[25–28] In 2006, Zeynizadeh and Setamdideh[29] reported a method for the reduction of nitroarenes with $NaBH_4$/charcoal in H_2O/THF. In 2012, Wang *et al.* reported a catalyst system for the reduction of nitroaromatics with $NH_2NH_2{\cdot}H_2O$ in the presence of mesoporous carbon.[30] Very recently, Zhou *et al.*[31] reported that AC, which was modified by chemical treatment in aqueous solutions of HNO_3, HCl and H_2SO_4, had been used as catalyst in the reduction of nitrobenzene using $NH_2NH_2{\cdot}H_2O$ as hydrogen donor due to the formation of an oxygen structure in the treated AC. It was reported by Pradhan and Sandle that the oxygen structure on the surface of the AC could be increased by oxidation with H_2O_2.[32] Considering the environmental problems, manufacturing cost and production safety, we have used H_2O_2-treated AC (H_2O_2-AC) and $NH_2NH_2{\cdot}H_2O$ (see SAFETY CAUTION in Experimental Section) as the catalyst system for reduction of nitroaromatic compounds to the corresponding amines. The results showed that the catalyst system could be used successfully without adding metal and could be reused several times without decreasing the catalytic efficiency.

Results and discussion

AC (20 g) was washed with deionised water three times and stirred with H_2O_2 (30%, 50 mL) overnight. The H_2O_2-treated AC was filtered, washed with deionised water until it gave a negative hydrogen peroxide test on starch–potassium iodide paper and then dried to powder under reduced pressure. The H_2O_2-AC was characterised by FTIR (Fig. 1).

As shown in Fig. 1, difference could be found between the AC before and after H_2O_2-treatment. In Fig. 1(2), the weak peak at 3172 cm^{-1} may be ascribed to hydroxyl groups and chemisorbed water. There is an increased relative intensity of the peak at 1605 cm^{-1} on H_2O_2-treatment, which may be consistent with an enhanced concentration of oxygen functional groups on the AC surface, which could improve the reduction efficiency for $NH_2NH_2{\cdot}H_2O$.[31,32]

The reduction of nitrobenzene was selected as the model reaction to optimise the reaction conditions (Scheme 1). For finding a suitable solvent, the reaction conditions were as follows: nitrobenzene (1.0 mmol), $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.) (see SAFETY CAUTION in Experimental section), H_2O_2-AC (10 wt%, 61.5 mg), solvent (1.5 mL), reaction temperature 40 °C and reaction time 10 h. As can be seen from Table 1 (entries 1–10), 10 kinds of solvent were tested. The highest isolated yield (81%) was obtained when using DMF as the reaction

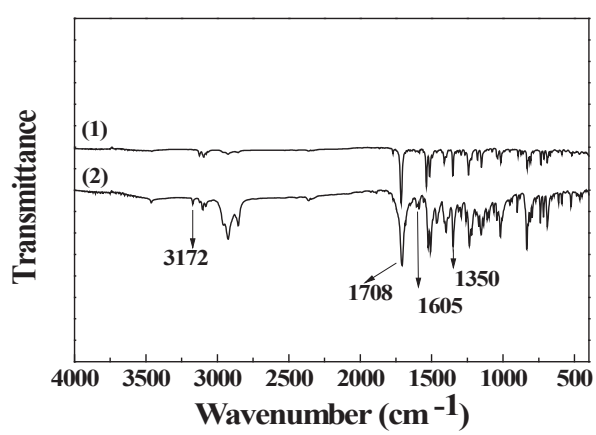

Fig. 1 FTIR spectra of ACs (1) before H_2O_2-treatment (2) after H_2O_2-treatment.

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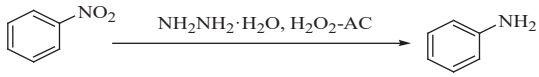


Scheme 1 Model reaction of reduction for optimising the reaction conditions.

Table 1 Effects of solvent and temperature on the model reaction[a]

Entry	Solvent	Temperature (ºC)	Time (h)	Yield (%)[b]
1	*n*-Hexane	40	10	30
2	Toluene	40	10	43
3	Acetonitrile	40	10	50
4	Dichloromethane	40	10	39
5	THF	40	10	73
6	Ethanol	40	10	70
7	Methanol	40	10	75
8	Water	40	10	60
9	1,4-Dioxane	40	10	19
10	DMF	40	10	81
11	DMF	60	10	87
12	DMF	80	10	92
13	DMF	100	10	99

[a]Reaction conditions: nitrobenzene (1.0 mmol), H_2O_2-AC (10 wt%), solvent (1.5 mL), $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.).
[b]Isolated yields.

Table 2 The recyclability of H_2O_2-AC[a]

Entry	Cycle	H_2O_2-AC (wt%)	Time (h)	Yield (%)[b]
1	1	50	3	99
2	2	50	3	99
3	3	50	3	98
4	4	50	3	99
5	5	50	3	99

[a]Reaction conditions: nitrobenzene (1.0 mmol), $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.), DMF (1.5 mL), 100 ºC.
[b]Isolated yields.

solvent (Table 1, entry 10). The lowest isolated yield (19%) was obtained when using 1,4-dioxane as the reaction solvent (Table 1, entry 9). Moderate isolated yields were obtained in THF, ethanol, methanol and water (Table 1, entries 5–8). Therefore, DMF was selected as the reaction solvent. Then, the model reaction was carried out in DMF at 60 ºC, 80 ºC and 100 ºC for 10 h and the corresponding isolated yields were 87, 92 and 99% respectively. This indicated that the higher the reaction temperature, the faster the reaction rate and the higher the isolated yield. Finally, 100 ºC was selected as the optimised reaction temperature.

For investigating the most suitable amount of H_2O_2-AC, the model reaction was carried out in DMF at 100 ºC for 3 h catalysed by different amounts of H_2O_2-AC (0 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt% and 60 wt%). As shown in Fig. 2, in the range from 0 to 50%, the more H_2O_2-AC used, the higher the isolated yield obtained. The result could be ascribed to increased oxygen structure in the catalyst. When 0 wt% H_2O_2-AC was used, there was no reaction. On continuously increasing the amount of H_2O_2-AC from 10 wt% to 20 wt%, 30 wt%, 40 wt% and 50 wt%, the obtained yields were 20, 47, 73, 85 and 99% respectively. When 60 wt% H_2O_2-AC was used, the same yield was obtained as that from 50 wt% H_2O_2-AC. When 50 wt% of unactivated carbon was used, the obtained yield was only 9%. Therefore, 50 wt% H_2O_2-AC was selected as the suitable catalyst loading.

In connection with the economic and environmental aspects, the lifetime and level of reusability of the H_2O_2-AC are very

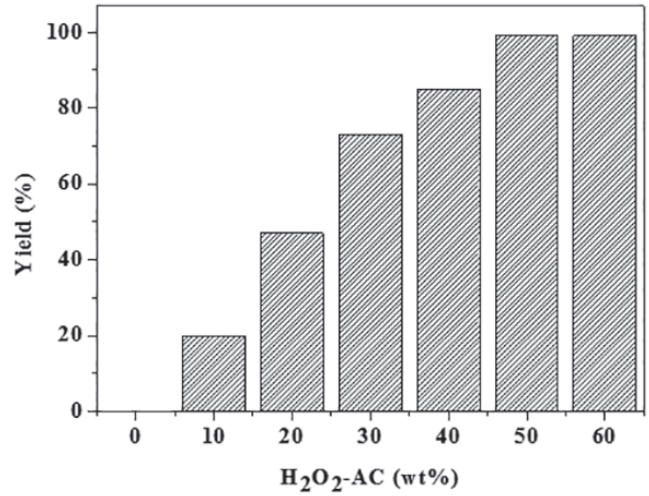
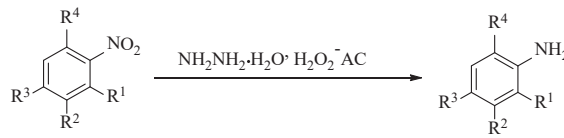


Fig. 2 Effects of amount of H_2O_2-AC on the yield of the model reaction in 3 h.

Table 3 Reduction of nitro compounds[a]



Entry	R^1	R^2	R^3	R^4	Time (h)	Yield (%)
1	H	H	H	H	3	100
2	Me	H	H	H	3	98
3	H	H	Me	H	3	100
4	Cl	H	H	H	3.5	97
5	H	Cl	H	H	3.5	98
6	H	H	Br	H	3.5	96
7	Cl	H	Cl	Cl	6	97
8	Me	H	H	Me	4	97
9	H	OH	H	H	5	99
10	H	H	OH	H	5	98
11	H	H	COOH	H	3	98
12	NH_2	H	H	H	5	92
13	H	H	NH_2	H	5	93
14	H	4-(3-Pyridyl) pyrimidine-2-amino	Me	H	3	100
15	H	$OCH_2CH_2OCH_3$	$OCH_2CH_2OCH_3$	$COOC_2H_5$	3	99

[a]Reaction conditions: nitro compounds (1 mmol), $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.), H_2O_2-AC (50 wt%), DMF (1.5 mL), 100 ºC.
[b]Isolated yields.

significant factors. The reusability of the H_2O_2-AC (50 wt%) was investigated by adopting the following procedure under the optimised conditions. After the completion of the reaction, the H_2O_2-AC was recovered by simple filtration and introduced into fresh DMF (1.5 mL) containing nitrobenzene (1.0 mmol) and $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.) for another reaction cycle. As can be seen from Table 2, the activity of the H_2O_2-AC was consistent after five cycles. No significant loss of H_2O_2-AC was observed.

Finally, to extend the general applicability of this protocol, a series of aromatic amines was synthesised using the optimised reaction conditions (Table 3). As can be seen from Table 3, the catalyst system had excellent selectivity and yields for the chemoselective reduction of various functionalised nitroaromatics under the optimised conditions. Interestingly,

halogen substituted nitrobenzenes were reduced to the corresponding chloroanilines in high yields and without any dehalogenation (Table 3, entries 4–7). The reducible functional group –COOH remained unchanged under the reaction conditions (Table 3, entry 11). The reduction reactions of nitroanilines gave the corresponding diaminobenzenes in excellent yields (Table 3, entries 12 and 13). To our surprise, this catalyst system was suitable for the reduction of *N*-(5-nitro-2-methylphenyl)-4-(3-pyridyl)pyrimidine-2-amine (Table 3, entry 14), which is an important intermediate in the manufacture of an anti-cancer drug named Imatinib. Our catalyst system has the advantage of higher purity, better yield and lower cost than other methods.[33–36]

Conclusion

In summary, an efficient and green protocol for the synthesis of aromatic amines from the corresponding nitroaromatic compounds with $NH_2NH_2{\cdot}H_2O$ catalysed by H_2O_2-treated AC in DMF at 100 ºC has been developed.

Experimental

All the chemicals were obtained from Tianjin Kermel Chemical Reagent Co. Ltd and were used as received. The H_2O_2-treated AC was characterised using FTIR (Thermo Nicolet Corporation NEXUS). The reactions were monitored by LC–MS (Waters/WATERS UPLC-TQD, Table 3, entries 2–6 and 8-15) and GC–MS (GCMS-QP2010 SE, Table 3, entries 1 and 7). The products were characterised using ^{1}H NMR (Bruker Avance/400 and Bruker Avance III HD/600) using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (*J*) in Hertz (Hz).

Preparation of activated carbon

AC (20 g) was washed with deionised water three times and stirred with 30% H_2O_2 (50 mL) overnight. Then the H_2O_2-treated AC was filtered off, washed with deionised water until it gave a negative hydrogen peroxide test on starch–potassium iodide paper and dried to powder under reduced pressure. Finally, 19.8 g of H_2O_2-treated AC was obtained.

Synthesis of amines; general procedure

CAUTION: Due precautions were taken with the handling and use of hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$) due to its toxicity.

A mixture of the organic nitro compound (1.0 mmol), $NH_2NH_2{\cdot}H_2O$ (2.5 equiv.) and H_2O_2-treated AC powder (50 wt%) in DMF (1.5 mL) was stirred vigorously magnetically at 100 ºC. The reaction was monitored by LC–MS or GC–MS. On completion the reaction mixture was filtered to remove the catalyst. The combined organic mixture material was dried using anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to obtain the products. All the compounds were known and characterised by their ^{1}H NMR and MS spectra and comparison with literature data.

Aminobenzene (*Table 3, entry 1*):[37] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.58 (s, 2H); GC–MS: $[M]^+$, *m/z* 93.

o-*Toluidine* (*Table 3, entry 2*):[38] Light-brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 2H), 4.18 (s, 2H), 2.20 (s, 3H); MS (ESI): $[M + H]^+$, *m/z* 108.

p-*Aminotoluene* (*Table 3, entry 3*):[39] Yellow–orange solid; m.p. 44-45 ºC (lit.[39] 40–44 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 3.54 (s, 2H), 2.28 (s, 3H); MS (ESI): $[M + H]^+$, *m/z* 108.

o-*Chloroaniline* (*Table 3, entry 4*):[40] Red oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.70 (t, *J* = 8.0Hz, 1H), 4.04 (s, 2H); MS (ESI): $[M(^{35}Cl) + H]^+$, *m/z* 128.

3-Chloroaniline (*Table 3, entry 5*):[37] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 2H); MS (ESI): $[M(^{35}Cl) + H]^+$, *m/z* 128.

4-Bromoaniline (*Table 3, entry 6*):[41] Brown solid; m.p. 65–68 ºC (lit.[41] 60–62 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 2H); MS (ESI): $[M(^{79}Br) + H]^+$, *m/z* 172.

2,4,6-Trichloroaniline (*Table 3, entry 7*):[42] Colourless solid; m.p. 72–74 ºC (lit.[42] 68–70 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 2H), 4.40 (s, 2H); GC–MS: $[M(^{35}Cl)]^+$, *m/z* 195.

2,6-Dimethylaniline (*Table 3, entry 8*):[37] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 8.0 Hz, 1H), 4.01 (s, 2H), 2.21 (s, 6H); MS (ESI): $[M + H]^+$, *m/z* 122.

m-*Aminophenol* (*Table 3, entry 9*):[39] Tan solid; m.p. 115–118 ºC (lit.[39] 119–120 ºC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.89 (s, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 8.4 Hz, 2H), 5.97 (d, *J* = 7.6 Hz, 1H), 4.86 (s, 2H); MS (ESI): $[M + H]^+$, *m/z* 110.

p-*Aminophenol* (*Table 3, entry 10*):[37,43] Brown solid; m.p. 193–196 ºC (lit.[43] 192–194 ºC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (s, 1H), 6.46 (d, *J* = 8.0Hz, 2H), 6.40 (d, *J* = 8.0 Hz, 2H), 4.38 (s, 2H); MS (ESI): $[M + H]^+$, *m/z* 110.

4-Aminobenzoic acid (*Table 3, entry 11*):[37,44] Pale yellow solid; m.p. 185–187 ºC (lit.[44] 186 ºC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.54 (d, *J* = 8.2 Hz, 2H), 5.87 (s, 2H); MS (ESI): $[M + H]^+$, *m/z* 138.

o-*Phenylenediamine* (*Table 3, entry 12*):[45,46] Colourless solid; m.p. 101–104 ºC (lit.[46] 98–100 ºC); ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.52 (s, 2H), 6.39 (s, 2H), 4.39 (s, 4H); MS (ESI): $[M + H]^+$, *m/z* 109.

p-*Phenylenediamine* (*Table 3, entry 13*):[39] Purple solid; m.p. 142–145 ºC (lit.[39] 141 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (s, 4H), 3.34 (s, 4H); MS (ESI): $[M + H]^+$, *m/z* 109.

N-*(5-amino-2-methylphenyl)-4-(3-pyridyl)pyrimidine-2-amine* (*Table 3, entry 14*):[47] Yellow solid; m.p. 145–148 ºC (lit.[47] 138–140 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.71 (d, *J* = 4.0 Hz, 1H), 8.49 (d, *J* = 4.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.42 (q, *J* = 4.0 Hz, 1H), 7.14 (d, *J* = 4.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 8.0 Hz, 1H), 3.30 (s, 2H), 2.24 (s, 3H); MS (ESI): $[M + H]^+$, *m/z* 278.

Ethyl 2-amino-4,5-bis(2-methoxyethoxy)benzoate (*Table 3, entry 15*):[48] Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (s, 1H), 6.14 (s, 1H), 5.58 (br, 2H), 4.31–4.26 (m, 2H), 4.14–4.11 (m, 2H), 4.08 (t, *J* = 4.5 Hz, 2H), 3.78 (t, *J* = 4.2 Hz, 2H), 3.72 (t, *J* = 4.5 Hz, 2H), 3.45 (d, *J* = 2.9 Hz, 6H), 1.36 (t, *J* = 7.1 Hz, 3H); MS (ESI): $[M + H]^+$, *m/z* 314.

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Electronic Supplementary Information

The ESI (^{1}H NMR spectra of the products) is available through http://ingentaconnect.com/content/stl/jcr/2017/00000041/00000009

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