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Advancement in methodologies for reduction of Nitroarenes

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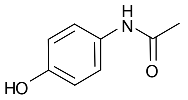
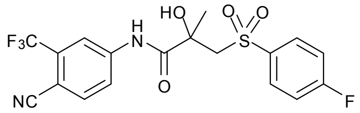
The importance of aryl amines as raw materials for varied applications has spurred extensive research in developing economic processes for reduction of nitroarenes. Developing green methodologies is now a compulsive discipline for synthetic organic chemists. Recent surge in nanochemistry has led to development of some interesting applications in nitro reduction processes. This review discusses some recent exemplary reports in this field. The different methods are classified based on the source of hydrogen utilized during reduction and the mechanism involved in the reduction process.

Synthetic chemistry plays a vital role in satisfying the huge demand for organic, inorganic or biochemical materials required for various important applications. Major problems in achieving this noble task are i) Energy expensive technologies; ii) Use of toxic solvents, reagents or catalysts; iii) Generation of harmful waste as by-products, etc.[1] Most of these issues are tackled in synthetic preparations and transformations by i) designing reactions maintaining the atom economy and minimum energy usage; ii) revealing domino processes; iii) improving the existing processes to minimize waste; iv) developing methods in energy efficient manner; v) exploring non-toxic recyclable catalyst; vi) replacing polluting solvent systems with aqueous medium for reactions and vii) using renewable sources of energy.[2, 1e-f, 1i]

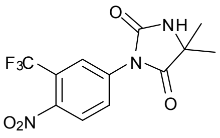
Aromatic amines are important intermediates in synthesis of several nitrogen containing biologically active compounds, agrochemicals, dyes, polymers, etc.[3] They are the precursors for many synthetically important intermediates like amides, imines, azo compounds, isocyanates and diazonium salts which could be converted to various other functional groups.[4] Anilines also form substructures of many pharmaceutical compounds (Figure 1). Paracetamol[5] **1a**, a widely used analgesic and antipyretic is an acetyl derivative of *p*-aminophenol. Bicalutamide[6] **1b** is a non-steroidal antiandrogen administered orally for the treatment of prostate cancer and hirsutism. This drug has a *p*-cyano-*m*-trifluoroaniline component in its structure. Nilutamide[7] **1c** having a *p*-nitro-*m*-trifluoromethylaniline core in its chemical structure is an antiandrogen used in treatment of advanced stage prostate cancer. Erlotinib[8] **1d** having an *m*-acetylenyl aniline and quinazoline component is a reversible tyrosine kinase inhibitor being used in treatment of non-small cell lung cancer and pancreatic cancer. Linezolid[9] **1e**, a synthetic antibiotic for multi drug resistant grampositive bacteria has *m*-fluoro-*p*-morpholinoaniline component. Fosamprenavir[10] **1f**, an anti-HIV drug and pro-drug of amprenavir has a *p*-sulfonamidoaniline unit in its structure.



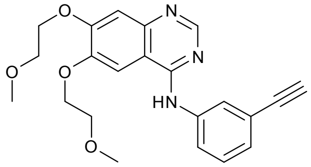
Paracetamol **1a**
(Analgesic)
(Antipyretic)



Bicalutamide **1b**
Anticancer (Prostate)



Nilutamide **1c**
Anticancer (Prostate)



Erlotinib **1d**
Anticancer (Lung/Pancreatic)

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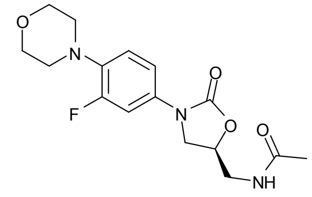
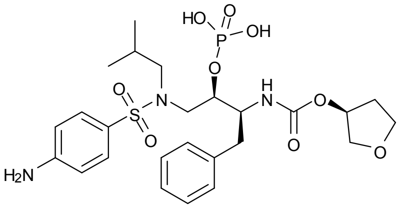


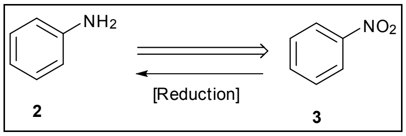
Linezolid **1e**
(Antibiotic)



Fosamprenavir **1f**
(AntiHIV)

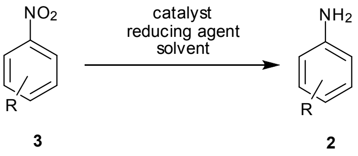
Figure 1: Medicinal compounds with aryl amine core structure

Reduction of nitroarenes is a most common, short and facile route employed to prepare anilines and is one of the areas where major part of recent published work is targeted (Scheme 1).[11,12] Synthetic chemists are now focusing on exploring new and efficient catalyst and developing simple and green procedure for this reaction. Selectivity in this reduction on larger scale is an important challenge in industrial processes.[13] Starting with Bechamp reduction,[14] a century back process where a lot of metallic waste is generated; recent advances provide methods using catalytic metal and clean reaction condition.



Scheme 1: Proficient approach for synthesis of aryl amine

Our interest in achieving reduction of nitroarenes and other green methodologies,[15] stimulated us to compile recent progresses and achievements reported for developing facile, energy efficient and green methodologies for reduction of nitroarenes (Scheme 2).



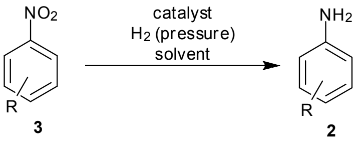
Scheme 2: Reduction of nitroarenes

The discussion is classified with respect to the use of reducing agents; such as molecular H_2, hydrides, hydrazine, *insitu* H_2 generation, metal reductants, redox systems, light induced electron transfer and biotic reduction as benign, clean, non-hazardous and non-polluting processes for reduction of nitroarenes.

1. Hydrogen gas
2. $NaBH_4$
3. Silyl hydrides
4. Hydrazine hydrate
5. *In situ* H_2 generation
6. Direct metal
7. MPV type redox processes using organic reducing agents (Transfer hydrogenation)
8. Light induced photo catalysis
9. Biotic reduction

1. Hydrogen gas

Molecular hydrogen in presence of metal/metal oxide can cause clean reduction of nitro group into amine along with water, a benign by-product. However, the formation of intermediates like *N*-phenylhydroxylamine (PHA), nitrosobenzene (NSB), azobenzene (AB), azoxybenzene (AOB) and hydroazobenzene (HAB) and their further conversion to amine is an integral part associated with such reductions. Metal leaching, recovery of catalyst, low catalyst loading, higher turnover cycle, use of benign solvent, low pressure conditions and compatibility of other functional groups are the problems to be addressed while designing a metal bound catalyst. Earlier reports have mostly used carbon as support where as newer supporting agents are now tried for efficient recovery and selectivity studies.[11d]



Scheme 3: Reduction of nitroarenes using Hydrogen gas

Table 1: Reduction methodologies using Hydrogen gas

Entry	Catalysts	H_2 (pressure)	Solvent, Conditions	Ref.
1	Fe_3O_4-NH_2-Pd	1 atm	EtOH, r.t.	16
2	Pd/Fe_3O_4	1 atm	EtOH/THF, r.t.	17
3	Polyurea entrapped Pd nanoclusters	1 atm	n-Hexanes, r.t.	18
4	Pd-B-mesoporous molecular sieve	20 atm	$scCO_2$, 50 °C	19
5	Colloidal gum acacia – Pt NPs	1 atm	water, r.t.	20
6	Pt/carbon nano tubes	1 atm	EtOH, r.t.	21a
7	Pt - multiwalled carbon nanotubes	40 atm	aniline, 60 °C	21b
8	Pt-N-heterocyclic carbene NPs	1 atm	THF, r.t.	22
9	Pt-ionic liquid	10 atm	90 °C	23
10	Pt- polysiloxane gel	10 atm	EtOAc, r.t. – 50 °C	24
11	Pt/SiO_2	1 atm	IPA, r.t.	25
12	Au-TiO_2	9 atm	toluene, 100 °C	26a
13	Au-TiO_2/ Au-Fe_2O_3	9-25 atm	toluene, 110 °C	26b
14	Au-organic-inorganic hybrid SiO_2	40 atm	EtOH, 100-140 °C	27
15	Au-ZrO_2	10atm	EtOH, 150 °C	28
16	Au-boronate NPs	5 atm	toluene, 100 °C	29
17	Pt-Au-TiO_2	10 atm	EtOH, 50 °C	30
18	Ag-CeO_2	6 atm	dodecane, 110 °C	31
19	Colloidal Ni-carboxymethyl cellulose	40 atm	H_2O-MeOH, r.t.	32
20	TiO_2/Ni-TiO_2	40 atm	H_2O-CO_2, 35 °C	33
21	Ni-SiO_2	20-30 atm	EtOH, 110 °C	34
22	Ru - reduced graphine oxide	20 atm	EtOH-H_2O, 110 °C	35
23	Mixed Ln-succinate-sulfate	5 atm	toluene, 90 °C	36

Magnetic catalyst has attracted considerable attention these days due to their ease of separation. Amine functionalized magnetic Fe_3O_4 nanoparticles (NPs) supporting 1.6 mol% Pd is developed as catalyst for reduction of aromatic nitro compounds to anilines using H_2 gas in ethanol at r.t. by Ma and coworkers.[16] Here magnetic separation helped in efficient recovery of the catalyst. Halogens (Cl, Br) or hydroxyl group bearing nitrobenzenes were selectively reduced to corresponding anilines with 92-99 % yield. The authors report no dehalogenated products. Compared to traditional reduction (10% Pd-C), which requires 2 h for completion, the reductions took place in shorter time (1 h) with less loading of Pd due to the activating effect of the amine functionality present on the support. The reduction of 1-nitronaphthalene took longer time (75 min). The catalyst showed excellent reusability for ten cycles with negligible leaching of the metal and TOF of 83.33 h^{-1}. This reduction system could also reduce the double bonds in stilbene, cinnamyl alcohol and methyl cinnamate. Heck reaction was also performed in excellent yield using this catalyst.

Pd supported on magnetic Fe_3O_4 is developed by Amali and Rana[17a] for selective reduction of chloronitroarenes. These systems showed TOF of 48.5 $h^{-1}$and negligible leaching even after 10 cycles. Similarly Pd(0) was immobilized with polyethyleneimmine on Fe_3O_4 NPs by Sun and coworkers.[17b] Low loading of Pd (0.25%) could also efficiently and selectively reduce 4-nitro acetophenone to 4-acetyl aniline. Former was also used for Suzuki reaction and latter for reduction of double and triple bonds as well as Suzuki-Miyaura reaction. The stability and efficient magnetic recovery of catalyst in turn helped in enhancing the reusability up to five cycles with slight decrease in activity. Palladium nanoclusters entrapped in polyurea prepared by Ji et al.[18] exhibit dual catalytic activity for reduction of nitro compounds and dehalogenation of aromatic chlorides in atmospheric hydrogen with 100% yield for reduction of nitro compounds at room temperature and >99% yield for dehalogenation of aromatic chlorides under refluxing methanol conditions. This immobilizing method was particularly effective and eliminated the need of special chelating groups. However, these authors have not addressed the usual selectivity study for problems of concurrent dehalogenation.

Supercritical CO_2 as a green solvent is used as along with Pd NPs supported on B-MCM-41 as catalyst and H_2 gas for hydrogenation of nitro aromatics by Chatterjee et al.[19] The *o*, *m* and *p*-chloronitrobenzenes (CNB) were reduced to the corresponding amine with high selectivity of >99% and conversion in the order of *p* >*m* >*o*. This system could also reduce a nitrile group and a phenol to cyclohexanone. However, in all the above cases selectivity in reduction between nitro and functional groups like olefin, aldehyde, cyano and benzyl ether was not studied.

Hydrogenation of nitroarenes is catalyzed by gum acacia supported Pt colloids with 0.24 mol % catalysts loading in water at r.t. using H_2 at 1 atm is described by Sreedhar et al.[20] This catalytic condition was inert to halogens, aldehydes and ketones with selective reduction of nitro group in 68 to 95 % yield. The yields were found to be consistent for 5 cycles with no leaching of metal.

Newer carbon supports have caught the fancy of people working in the field of catalysis. Pt supported on carbon nanotubes (Pt/CNT) and PtM/CNT (M = Mn, Fe, Co, Ni and Cu) is studied as catalyst for selective hydrogenation of *m*- and *o*-CNB to corresponding chloroanilines by Han and Li.[21a] All metals studied except Cu was found to enhance the catalytic behavior of Pt/CNT and PtFe/CNT was found to be the best. Solvent free selective hydrogenation of nitrobenzene to aniline using ultrafine Pt deposited on carbon nanotubes is reported by Sun et al.[21b] High turnover frequency (69,900 h^{-1}) without accumulation of PHA is noteworthy in this process. However reusability, metal leaching and selectivity to other functional groups are not studied with this process.

Chaudret et al. have described the chemo selective reduction of series of functionalized nitroarenes with H_2 gas (1 bar) at r.t using Pt NPs stabilized with N-heterocyclic ligands as catalyst.[22] Sensitive functionalities such as carbonyl, olefins as well as halogens were tolerated in this reduction. Ethyl-4-nitrocinnamate was reduced with 79% selectivity, 4-chloronitrobenzene with 95%, 4-nitrobenzaldehyde with 94% and 3-nitropyridine with >99% selectivity.

Ionic liquids (IL) are pursued as green alternative for toxic volatile solvents. Ionic-liquid-like copolymer stabilized Pt nano catalysts are studied for selective hydrogenation of 2,4-dichloro-3-nitrophenol to 2,4-dichloro-3-aminophenol using H_2 gas in different IL by Yuan et al.[23] The IL system containing an alcohol group displayed better selectivity, recyclability (9 times) and higher turnover number (2075).

Polysiloxane gels containing Pt species, [Pt]@SiC_6 and [Pt]@SiC_6-TAA, were demonstrated by Nagashima and coworkers as recyclable heterogeneous catalysts for reduction of various nitro compounds to their corresponding amines with other functional groups (ester, ketones, benzyl ether, benzyl alcohol, amide and chloro) remaining intact.[24] Turnover number up to 10,000 was achieved, the catalyst recovery/reuse was done for five times and metal leaching was beyond detection limits. Aliphatic nitro groups were reduced rather slowly at room temperature.

Substituted nitro aromatics were selectively hydrogenated to the corresponding N-aryl hydroxylamines in excellent yields (up to 99%) using supported platinum catalysts such as Pt/SiO_2 under a hydrogen atmosphere (1 bar) at room temperature by Takenaka et al.[25] This reduction was carried out in IPA with DMSO and n-$BuNH_2$ as additives.

Chemical community had ignored gold due to its low reactivity but recently its unique catalytic properties have drawn the attention of numerous research groups, which has been reflected in a number of research publications in the literature.

Chemoselective reduction of nitroarenes containing double bonds, carbonyl, nitrile or amide groups on supported gold NPs (Au/TiO_2 and Au/Fe_2O_3), using a batch reactor under H_2 pressure was demonstrated by Corma et al.[26a] This group also used Au on TiO_2 as a hydrogenation catalyst to prepare azo compounds directly from nitroaromatics through a two-step (hydrogenation followed by aerobic oxidation), one-pot, one-catalyst reaction.[26b]

Highly dispersed gold NPs supported on organic–inorganic hybrid silica were shown to exhibit good catalytic activity and stability for liquid phase catalytic hydrogenation of aromatic nitro compounds by Tan et al.[27] *p*-CNB was reduced with 80% selectivity with significant amount of *p*-chloro nitroso intermediate remaining. Similarly hydrogenation of CNBs to chloroanilines is reported over Au/ZrO_2 catalyst with H_2 gas in ethanol by He et al.[28] with complete selectivity. Recently, gold NPs embedded in boronate self-assemblies were used for selective reduction of 4-nitrostyrene using H_2 gas.[29] Adding small amounts of Pt entities (0.01–0.03 wt%) onto the Au surface of a Au/TiO_2 catalyst was shown to be an efficient approach to improve the catalytic activity of Au for the hydrogenation of *p*-CNB by He et al.[30], where the C–Cl bond remained intact. Excess amounts of Pt (>0.03 wt%) and high reaction temperatures causes the occurrence of the undesired catalytic hydrodechlorination reaction of *p*-CNB. Reusability of this catalyst system was demonstrated for five cycles without leaching any of the metals.

Ag@CeO$_2$ core shell nano composite is used as catalyst for reduction of nitro compounds to anilines by H_2 gas by Kaneda and coworkers.[31] This catalyst helped to achieve complete selectivity towards nitro reduction in presence of double bond with > 95 % yield. Selectivity in presence of other functional groups particularly like halo or aldehyde would have been interesting but appears to have been not studied. This system could also reduce oxiranes to alkenes.

Among the coinage metals Ni is preferred over other metals because of its low cost. A biopolymer-inorganic catalyst system involving colloidal Ni and carboxymethylcellulose is reported for reduction of nitroaromatics using H_2 gas at r.t. in MeOH-water mixture by Ali and co workers.[32] Various aniline products were obtained with substrate: catalyst ratio (100:1) and 40 bar H_2 gas in 79-96 % yields. Reduction was achieved in presence of ester, OH and NH_2 groups on aromatic ring. This system was also useful for reduction of ketone to 2° alcohol. Low pressure CO_2-water system with Ni is applied for reduction of nitrobenzene to aniline by Arai and coworkers.[33] Ni was supported on Al_2O_3 for this reduction. Similarly CNB was reduced to chloroaniline with Ni/TiO$_2$ in low pressure CO_2 (3MPa) – water system by the same group. Zheng et al. [34a] have described Ni/SiO$_2$ catalyst for selective reduction of nitroarenes to anilines using H_2 gas wherein ketones, aldehydes, chloro and amide functionalities were found to be unaffected. Magnetic recovery and reusability of this supported catalyst was also demonstrated for five cycles. H. Jiang's group has recently presented an one-pot synthesis of Ni-Ni-Fe$_2$O$_4$/carbon nanofiber composites from biomass and utilized them as catalyst for selective hydrogenation of aromatic nitro compounds with hydrogen gas.[34b]

Graphene and graphene-oxide materials are studied for various applications in material science and this trend has been followed even in catalysis because of their applications as support and also its ability to enhance the property exhibited by the catalyst.

A reduced graphene oxide (RGO) supported-ruthenium (Ru) catalyst was prepared by Wang et al. and applied for the selective hydrogenation of *p*-CNB to *p*-chlroaniline, exhibiting a turnover frequency (TOF) of 1800 h^{-1} and a selectivity of 99.6 % at complete conversion of *p*-CNB. Ketone functionality was also well tolerated during the reduction.[35] Here Ru NPs were in an electron-deficient state due to the electron transfer between the NPs and the RGO sheets. No loss in efficiency of this catalyst system was observed for ten runs with minimal leaching of Ru (0.2%)

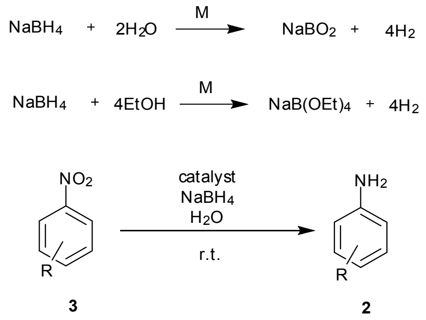
Mixed lanthanide succinate–sulfate isostructural 3D polymeric metal–organic frameworks monoclinic space group have also been used for reduction of the nitro group by Monge and coworkers.[36]Other reducible groups like aldehyde, cyano, halo (Br, I) remained unaffected during the reduction.

Though catalytic hydrogenation is routinely employed in industry and in research laboratories, it has distinct disadvantage of requirement of special equipments to handle high pressure and inflammability of H_2. Also large amount of hydrogen is wasted and is usually let off in atmosphere after the reaction is over.

2. NaBH$_4$

Insitu generation of hydrogen during reduction process can avoid use of sophisticated equipments required for handling hydrogen gas and wastage due to excess use of gas under pressure. $NaBH_4$ has been employed as a clean source of hydrogen generation in fuel cells using different metal bound catalyst. The same system could also be used for reduction of nitro to amine functionality with formation of non-toxic sodium borate as a by-product.

Ease of handling $NaBH_4$ is also an added advantage in this process. The functional groups which get reduced with $NaBH_4$ are usually intolerable during usage of this reduction process.



Scheme 4: Reduction of nitroarenes using $NaBH_4$ (3-5 equiv)

Table 2: Reduction methodologies using $NaBH_4$

Entry	catalyst	Ref.
1	Pd-poly-(*3,4*)-ethylenedioxy-thiophene matrix	37
2	Pd (II) phthalocyanine [a]	38
3	Au-Fe_3O_4 nanocatalyst	39a
4	Cu(II) silica @ Fe_3O_4 composites	39b
5	Au-Nano Active MgO Plus	40
6	Au nanorods, KBH_4	41
7	Au-epigallocatechin-*3*-gallate-collagen fiber	42
8	Au-resorcinarene NPs	43
9	Au-alumina/membrane	44
10	Au-boronate NPs	30
11	Au-double hydrophilic block copolymer	45
12	Au-graphene hydrogel	46
13	Au-TiO_2,[b]	47
14	Ag-halloysite nanotubes	48
15	Ag quantum clusters	49
16	Ag-Au-Fe_3O_4-carbon composite	50
17	Ag-graphite-poly-(amidoamine)-dendrimer	51
18	Hollow Ag nanospheres	52
19	(Pt/Au) NPs	53
20	$CuBr_2$[c]	15b
21	Cu NPs	54a
22	Cu-Ferrite graphene hybrid	54b
23	Pd/Cu/graphene	54c
24	Cu/MIL-101(Cr) nanocomposites	55
25	Co_3S_4	56
26	Co-Co_2B[d]	15c

[a]EtOH,100 °C; [b] NH_3BH_3, EtOH; [c] EtOH, [d] MeOH

Synthesis of Pd incorporated poly-(3,4)ethylenedioxythiophene (PEDOT) matrix in aqueous medium was achieved and its catalytic activity was demonstrated using a model reaction, i.e. reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ by Harish et al.[37a] Similar solid supported Pd(0) catalyzed highly chemoselective reduction of nitroarenes to the corresponding anilines was accomplished in MeOH-H_2O mixture by Shil et al.[37b] This catalyst showed high compatibility with various reducing agents like $NaBH_4$, Et_3SiH, and $NH_2NH_2.H_2O$ and a large number of reducible functional groups such as sulfonamide, amides, carboxylic acid, ester, alcohol, halide, heterocycle, nitrile, alkene, carbonyl, *O*-benzyl, and N-benzyl were tolerated.

Pd (II) phthalocyanine were also used with low catalyst loading up to 1 mol% along with $NaBH_4$ in EtOH by Verma et al.[38]

Dumbbell and flower-like Au-Fe_3O_4 heterostructures have been fabricated by thermal decomposition of the iron oleate complex in the presence of Au NPs using different sizes of Au NPs as the seeds and employed as magnetically recyclable catalyst (for *p*-nitrophenol and 2,4-dinitrophenol reduction) by Lin and Doong.[39a] Similarly, Cu(II)-NPs on silica Fe_3O_4 support was used for reduction of nitroarenes with $NaBH_4$ in aqueous medium at r.t. by Sharma et al.[39b] Other reducible moieties like CN and halides were retained during reduction.

Nanocrystalline magnesium oxide supported gold NPs are used as recyclable heterogeneous catalyst for reduction of nitroarenes to anilines using sodium borohydride in double distilled water at room temperature by Maheswaran and coworkers.[40] This reduction system could tolerate varied substitution of aromatic ring like F, Cl, Br, I, OCH_3, COOMe, vinyl, CN, OH and NH_2. After the reduction the spent catalyst could be recycled by centrifugation and reused. There was slight loss in recovery, which resulted in marginal decrease in efficiency.

Uniform-sized gold nanorods have been prepared by Bai et al.[41] *via* a three-step seed-mediated growth method using a long-chain ionic liquid (IL, C_{12}mimBr) as a capping agent and exhibited excellent catalytic efficiency for the reduction of *p*-nitrophenol and *p*-nitroaniline. Size-controlled Au NPs supported on collagen fiber (CF) are prepared by Shi and coworkers.[42] Epigallocatechin-3-gallate (EGCG), a typical plant polyphenol, was grafted onto CF surface to serve as reducing/stabilizing agent, so that the Au NPs were generated on CF surface without introduction of extra chemical reagents or physical treatments. This stabilized Au NPs were found to be active heterogeneous catalysts for the reduction of 4-nitrophenol to 4-aminophenol in aqueous phase. The catalyst was recovered simply by filtering and successfully used for 20 cycles with conversion of >98%.

Resorcinarene-functionalized Au NPs were prepared in aqueous solution in the presence of amphiphilic tetramethoxyresorcinarene tetraaminoamide by Yan and coworkers.[43] The catalytic activity of the obtained Au NPs for the reduction of aromatic nitro compounds was investigated. Layer-by-layer deposition of polyelectrolyte/Au NP films in porous alumina, track-etched polycarbonate and nylon substrates gave catalytic membranes that showed high catalytic activity in the selective reduction (98 %) of *p*-nitroaromatic compounds containing cyano, chloro, and vinyl with sodium borohydride is described by Bruening and coworkers.[44] The reduction nitrocyclohexane resulted in incomplete reduction giving corresponding nitroso (73%) and amine (27%) compounds.

4-Nitrophenol was reduced with $NaBH_4$ using Au-boronate NPs.[29] Water-dispersible Au NPs using a double hydrophilic block copolymer (DHBC), poly(ethylene oxide)-block-poly(acrylic acid) (PEO-b-PAA) as a template were prepared and found to be highly effective in catalyzing the reduction of a series of nitroarenes by Kim and coworkers.[45]However selectivity studies were not performed with this catalyst system.

A cylindrical piece of Au/graphene hydrogel, 1.08 cm in diameter and 1.28 cm in height, has been synthesized through the self-assembly of Au/graphene sheets under hydrothermal conditions by Li et al.[46] The hydrogel, containing 2.26 wt% Au, 6.94 wt% graphene, and 90.8 wt% water, exhibited excellent catalytic performance towards the reduction of 4-nitrophenol to 4-aminophenol. The high catalytic activity arises from the synergistic effect of graphene: (1) the high adsorption ability of graphene towards 4-nitrophenol, providing a high concentration of 4-nitrophenol near to the Au NPs on graphene; and (2) electron transfer from graphene to Au NPs, facilitating the uptake of electrons by 4-nitrophenol molecules.

Quantitative reduction of nitroarenes into anilines and nitroalkanes into alkylhydroxylamines by the ammonia borane complex was achieved using gold NPs supported on titania catalyst, even at a ppm loading level by Stratakis and coworkers.[47] Reducible functional groups like benzyl ether, halo (Cl, Br), ester and nitrile groups remained intact while aldehyde and keto group got reduced. In case of 3-nitrostyrene 10% over reduction of the double bond was observed. Inert atmosphere is required for this reduction process to avoid formation of minor amounts of azoxyarenes. The authors have proposed a mechanism based on evidence obtained that amines are obtained from hydroxylamines without intervention of nitrosobenzene via gold hydride species.

The silver NPs supported halloysite nanotubes (Ag/HNTs), with Ag content of about 11%, were used for the catalyzed reduction of 4-nitrophenol with $NaBH_4$ in alkaline aqueous solutions by Liu and Zhao.[48] Quantum clusters (QCs) of silver such as $Ag_7(H_2MSA)_7$, $Ag_8(H_2MSA)_8$ (H_2MSA, mercaptosuccinic acid) were synthesized by the interfacial etching of Ag NP precursors and were loaded on metal oxide supports to prepare active catalysts such as $Al_2O_3@Ag_{7,8}$, $SiO_2@Ag_{7,8}$, $TiO_2@Ag_{7,8}$, and $Fe_2O_3@Ag_{7,8}$ by Pradeep and coworkers.[49] These catalysts showed enhanced catalytic activity for the reduction of nitrophenols to aminophenols.

The heterostructure Ag–Au bimetallic nanocrystals supported on Fe_3O_4@carbon composite microspheres were synthesized by facile and controllable approach by Guo and coworkers,[50] wherein the Ag nanocrystals attached on the Fe_3O_4@carbon microspheres were prepared first and served as reductant for the galvanic replacement reaction with the Au precursor ($HAuCl_4$). They could give high yields for reduction of substituted nitroaromatic compounds, irrespective of the linked electron-donating or electron-withdrawing groups.

Hyperbranched polyamidoamine (PAMAM) dendrimer were grafted on the graphite surface and Ag NPs were synthesized within the graphite grafted PAMAM dendrimer templates and applied as nanocatalyst for the reduction of nitro aromatics by Rajesh and Venkatesan.[51] The efficiency of this system has been demonstrated through the reduction of halonitroarenes without dehalogenation in the halo-substituted nitro benzenes and selective reduction of nitro groups in the presence of imine functionality under mild condition.

Hollow silver nanospheres colloids were prepared by a simple reaction of silver nitrate ($AgNO_3$), sodium hydroxide (NaOH) and hydroxylammonium hydrosulfate ($(NH_2OH)_2 \cdot H_2SO_4$) in the presence of gelatin by Parikh and coworkers.[52] Superior catalytic performance was observed in 4-nitrophenol to 4-aminoaniline reduction in the presence of freshly prepared ice cold aqueous solution of sodium borohydride at room temperature.

Catalytic reduction of 4-nitrophenol by sodium borohydride was achieved by Ballauff and coworkers in the presence of Pt/Au NPs embedded in spherical polyelectrolyte brushes, which consist of a polystyrene core onto which a dense layer of cationic polyelectrolyte brushes are grafted. The average size of these NPs was approx. 2 nm.[53]

We have reported Copper(II) bromide as a procatalyst for the in situ preparation of active Cu NPs for the efficient reduction of nitroarenes using sodium borohydride.[15b] Acid, chloro, hydroxyl, benzyl ether and amino functionality remained intact while the olefin and cyano were affected.

Gradzielski and Mehta et al.[54a] synthesized copper NPs using poly acrylic acid and utilized them for catalytic reduction of 4-nitrophenol to 4-aminophenol. The activity was found to increase as the particle size decreased. Super paramagnetic Cu-ferrite-graphene hybrid nanocomposites were used for reduction of nitroarenes by Wang and coworkers.[54b] The ferrite component helped in efficient recovery without loss in catalytic activity. Pd-Cu NPs supported as graphene were used by Feng et al. for chemoselective reduction of nitroarenes with $NaBH_4$ in presence of CN, ester, halogens, etc.[54c] Cu nanostructures of various shapes and sizes such as nanospheres, nanowires and nanorods were synthesized by R. Kaur and B. Pal and their catalytic activities were studied for nitro-aromatic reduction.[54d] Cu nanowires (length ≈ 4–6 µm and width ≈ 60–80 nm) were found to exhibit superior catalytic activity. Similarly 3-nitro-4-methoxy-acetylaniline was selectively reduced by Y. Feng et al. to 3-amino-4-methoxy-acetylaniline using Cu NPs as catalyst and $NaBH_4$ as hydrogen source in water.[54e]

Wu et al.[55] loaded Cu NPs on a MIL-101 (Cr) metal–organic framework which showed enhanced catalytic activity for the reduction of aromatic nitro compounds.

Cobalt sulfide Co_3S_4 is recently reported for such reduction using $NaBH_4$ in EtOH under sonication.[56] The halogens were unaffected during this nitroreduction.

Magnetically recoverable and recyclable Co–Co_2B nanocomposites are described for the catalytic and chemoselective reduction of nitroarenes using sodium borohydride from our laboratory.[15c] Halogens, benzyl ether and acid functionality remained undisturbed while cyano and aldehyde group got reduced.

Though $NaBH_4$ mediated reductions are safer to handle comparative to catalytic hydrogenations, they have the problem of work up to extract the product form the aqueous reaction medium. Also excess of $NaBH_4$ is required to complete the reduction process. Further metal on reaction with $NaBH_4$ generates hydrogen, which needs to be taken care when large-scale reductions are to be carried out. Also in most of the above cases the selectivity problem is not addressed rather the work centered on making NPs and to demonstrate the usefulness of the NPs for the catalytic process.

3. Silyl Hydrides

Nitro reduction with silyl hydrides persuade through nitroso and hydroxylamines route, the exact mechanism for this reduction process is not clear. It may take place via metal catalyzed hydrosilylation or via hydrogenation with evolved hydrogen gas.

As early as in 1973, Lipowitz and Bowman reported the first example of polymethylhydrosiloxane (PMHS) mediated Pd/C catalyzed reduction of nitrobenzene to aniline.[57a] A combination of $Pd(OAc)_2$, aq. KF and PMHS is reported for reduction of aromatic nitro groups to amines at room temp. in high yields with wide functional group tolerance and short reaction times by Rahaim Jr. and Maleczka Jr.[57b] Steric hindrance by one *ortho* substituent did not slow the reduction process while two *ortho* substituents did. Electron donating groups were well tolerated except for 4-nitro-thio-anisole (10 % yield) while 2-nitrothiophen was reduced successfully. Electron withdrawing groups like acid, ester, amide, benzylic ketone, fluoro and trifluoro were unaffected. Presence of nitrile group (*o*, *m*) required longer times to form the corresponding amino nitriles while reduction of *p*-nitrobenzonitrile stopped at the *p*-(hydroxyamino)benzonitrile. Selectivity in the reduction of 4-nitrobenzaldehyde was 73% and 1,4-dinitrobezene was 72%. Interestingly TBS protected nitrophenol was reduced selectively

3 2

Scheme 5: Reduction of nitroarenes using silyl reagents

Table 3: Reduction methodologies using silyl reagents

Entry	Catalyst	Silanes (equiv)	Solvent/ conditions	Ref.
1	$Pd(OAc)_2$	PMHS (4)/KF	THF/H_2O, r.t.	57
2	$ReOCl_3(PPh_3)_2$	$PhMe_2SiH$ (36)	toluene, 110 °C	58
3	$Fe(acac)_3$	TMDS (4)	THF, 60 °C	59
4	$FeBr_2$, PPh_3,	$PhSiH_3$ (2.5)	toluene, 110 °C	60
5	Fe(II)phthalocyanine	Ph_2SiH_2 (3)	EtOH, 100 °C	38
6	Au-Fe_3O_4	TMDS (4-10)	EtOH, r.t.	61

(93%) inspite of the presence of KF. However complete dehalogention was observed for chloro-bromo nitrobenzenes while aliphatic bromide remained intact. Olefin remained unaffected during the course of reaction. Methyl 5-nitro-2-furanoate was reduced successfully whereas for the reduction of 5-nitrobenzamidazole required modification in the protocol sequence. Aliphatic nitro groups (primary and secondary) were reduced to hydroxylamines with same system by replacing PMHS/KS with triethylsilane.

Alternatively, the reduction of aromatic nitro compounds to the corresponding amines with silanes catalyzed by high valent oxo-rhenium complexes is reported by Fernandes and coworkers.[58a] The catalytic systems $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) and $PhMe_2SiH/ReOCl_3(PPh_3)_2$ (5 mol %) reduced efficiently a series of aromatic nitro compounds in the presence of a wide range of functional groups such as ester, halo, amide, sulfone, lactone, and benzyl. This methodology also allowed the regioselective reduction of dinitrobenzenes to the corresponding nitroanilines and the reduction of an aromatic nitro group in presence of an aliphatic nitro group. Similarly, Wilkinson's catalyst, $RhCl(PPh_3)_3$ was also used along with Et_3SiH in refluxing toluene for reduction of nitroarenes.[58b]

1,1,3,3-Tetramethyldisiloxane (TMDS)/$Fe(acac)_3$ was used for nitroreduction and the product amines were isolated as hydrochloride salts with good to excellent yields by Lemaire and coworkers.[59] Nitrile, acid, ester and bromo groups were well tolerated while *p*-nitrobenzaldehyde gave *p*-hydroxymethylaniline. *m*-Dinitrobenzene was selectively reduced to *m*-nitroaniline.

Iron-based catalytic system consisting of $FeBr_2–Ph_3P$ has been discovered for the reduction of nitroarenes with organosilanes by Beller's.[60] Except for fluorine substituent high yields of anilines were obtained for halonitrobenezes without significant amount of dehalo products. The catalyst also showed selectivity in challenging substrates with C=O, C≡N, C=C, and NO_2 groups. However, hydrosilylation failed in the case of 3-nitrostyrene and 4-nitrophenylacetate.

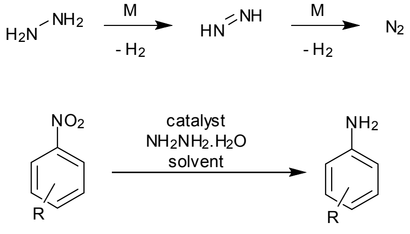
Fe (II) Phthalocyanines were also used with diphenylsilane as hydrogen source in refluxing ethanol.[38] This method was applied on gram scale conversion of *p*-nitrotoluene to *p*-toluidine.

Magnetically separable gold-nanoparticle catalyst was prepared and it showed excellent activity for chemoselective reduction of nitroarenes with hydrosilanes.[61] Selective reduction 4-fluoro- and 4-chloronitrobenzene required mere 1 mol% Au while 40 mol% was required for complete reduction of 4-bromonitrobenzene and 4-iodonitrobenzene failed to get reduced. Ketone, ester, amide, cyano, alkene, benzyloxy and carbobenzyloxy functional groups survived during nitro reduction. The activity of the catalyst reduced during its reuse but increasing the quantity of reducing agent could compensate this reduced activity.

Again like $NaBH_4$ mediated reductions the problem of work up, scaling up and use of excess reducing agent cannot be avoided for this system. However the selectivity in the reduction process looks to be promising and further developments are expected.

4. Hydrazine hydrate

Hydrazine hydrate is known to decompose in presence of trace amount of transition metal to hydrogen and benign N_2 gas. The *in situ* generation of hydrogen gas on the active metal surface thus facilitates the reduction process.
The hydrogen release from this reaction can be used for reduction process while avoiding elaborate hydrogenation apparatus required for hydrogen gas. However, the toxicity and its well known use as rocket fuel may have to be taken into account during large scale reduction processes.



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Scheme 6: Reduction of nitroarenes using hydrazine (1.2-10 equiv)

Table 4: Reduction methodologies using hydrazine

Entry	catalyst	Solvent/conditions	Ref.
1	PEG-35k-Pd NPs	90 °C	62
2	Pd-C nanospheres	$EtOH:H_2O$, 80 °C	63
5	Fe_3O_4 NPs	EtOH, 80 °C	64a
3	$Fe(acac)_3$	MW, 150 °C	64b
4	Graphene-Fe_3O_4	70 °C	65

6	Iron oxide hydroxide, polymer supported NH_2NH_2	iPrOH, 80 °C	66
7	$FeSO_4$ –Fe phthalocyanine	EtOH:H_2O, 120 °C	67
8	Rh-Fe_3O_4	EtOH, 80 °C	68
9	Hollow Rh nanocomposite	EtOH, 80 °C	69
10	Rh-porous ionic copolymer	EtOH, 60 °C	70
11	Zn-phthalocyanine	PEG-400, 100 °C	71
12	Zn or Mg, Hydrazine glyoxalate	r.t.	72
13	Co-Co_2B	MeOH, r.t.	15c
14	$(Bu_4N)[Ni(toluene\text{-}3,4\text{-}dithioalate)_2]$	THF, reflux	73
15	MoS_2	toluene, 60-80 °C	74
16	PVP stabilized Ni or Co	H_2O r.t.	75a
17	Co-Mo_2C/activated carbon	Reflux	75b
18	Carbon/Graphite	iPrOH, reflux	75c
19	Multiwalled carbon nanotubes	EtOH, 100 °C	76a
20	Boron-Pyrolytic graphene oxide	90 °C	76b

Polymeric PEG-35K-Pd NPs were used by Yadav et al. for reduction of nitro compounds to amines with hydrazine hydrate as a reducing agent at 90 °C.[62] This reduction method was inert to halogens giving haloanilines in quantitative yield. The catalyst was recycled by centrifugation and could be used to maximum 8 cycles.

Palladium NPs immobilized on carbon nanospheres are reported to catalyze reduction of nitroaromatic compounds with 1.36 % Pd using hydrazine hydrate in ethanol-water mixture is described by Yu et al.[63a] The authors claim that they could selectively reduce nitro group in presence of other reducible vinyl and aldehyde groups. It may be noted that no hydrazone product or the alcohol product is reported though hydrazine was used in excess (1:10 mol ratio). The low Pd loading (1.36 %) also helped to retain halogen in the reduced products. In case of 3-nitrophenol and 4-methyl nitrobenzene the main byproducts were corresponding azo and azoxy intermediates. Similarly Pd/C is also studied for selective reduction of halogenated nitrobenzenes using hydrazine hydrate under reflux or MW conditions by Li and coworkers.[63b]

Readily available and magnetically separable Fe_3O_4 NPs were utilized for recyclable and efficient nitroarene reduction.[64a] Reducible functional groups like halogens, ester, benzyloxy ether, amide and benzyl alcohol remained intact while only 45 % selectivity was obtained for the reduction of ethyl 4-nitrocinnamate. Aliphatic nitro compounds were reduced less efficiently.

In situ generated iron oxide nanocrystals are used for reduction of nitroarenes using MW irradiation by Kappe's group.[64b] This method using hydrazine hydrate as reducing agent yielded anilines in quantitative yields without affecting halogens, esters, amides or nitriles. Reusability studies suggested that it is effective for 3 cycles. The authors also demonstrated that the reduction could be carried out in a continuous flow method on industrial scale. After the reduction process the colloidal Fe_3O_4 nanocrystals agglomerate and can be selectively removed by using a simple magnet.

Graphene-Fe_3O_4 nanocomposite (G-Fe_3O_4) and superparamagnetic graphene-Fe_3O_4 nanocomposite (G- Fe_3O_4) were synthesized by a chemical co-precipitation method and used as an efficient catalyst for the reduction of nitroarenes with hydrazine hydrate by Zhang et al., Wang and coworkers and Shokouhimehr et al.[65] 4-CNB was selectively reduced without any dehalogenation. The catalytic activity did not decrease to any extent in the five cycles studied.

Iron oxide hydroxide catalyst was used for reduction of nitroarenes to anilines with polymer (D113, macroporous weak acidic ion-exchange resin) supported hydrazine hydrate in refluxing isopropanol by Shi and coworkers.[66] Anilines were obtained in 93 to 99 % yields without affecting chlorides and esters.

Iron phthalocyanine and iron sulfate catalyzed reduction of nitroarenes to anilines is reported with hydrazine hydrate as hydrogen source in mixture of water and ethanol by Sharma et al.[67] This method was applied on gram scale to substrate with substituent like acid, nitrile, sulfonamide, hydroxyl, *O*-benzyl, *N*-benzyl, lactones, etc. 4-Chloro-2-nitrophenol was selectively reduced to corresponding aniline without affecting other functionalities. Also other heterocyclic nitro- compounds like nitro-isoquinoline, nitro-indole, nitro-thioindole, etc. were successfully reduced to corresponding amines.

Rh–Fe_3O_4 heterodimer nanocrystals were prepared by controlled one-pot thermolysis. The nanocrystals exhibited excellent activities for the selective reduction of nitroarenes and alkenes by Hyeon et al.[68] Hollow Rh nanocomposites also showed similar results.[69] A highly active and selective Rh/highly porous ionic copolymer (PICP) nanocatalyst for the reduction of nitroarenes into corresponding anilines with hydrazine monohydrate under mild conditions is also reported by Luo et al.[70] The halo nitrobenzenes were reduced successively without any dehalogenated products.

Zn Phthalocyanine was used as catalyst (1 mol%) for reduction of aromatic nitro compounds to anilines using $N_2H_2.H_2O$ as reducing agent and PEG-400 as solvent by B. Singh and co workers.[71] Various functional groups like acid, ester, amide, sulfonamide, cyano, halogens, benzyloxy and benzyl amines were unaffected in this nitro reduction. 3-Nitrostyrene, 1,3- and 1,4-dinitrobenzenes were reduced selectively while 1,2 dinitrobenzene showed moderate conversion (58%). Exclusive formation of benzotriazole was obtained when excess hydrazine hydrate was used during reduction of 1,2-dinitrobenzene. Aromatic nitro compounds were selectively and rapidly reduced at r.t. to corresponding amines in good yields by employing hydrazine glyoxalate in presence of Zn or Mg powder by Raju et al.[72] Halonitrobenzenes were reduced to corresponding amino benzenes without dehalogenation. *p*-Nitrocinnamic acid is reduced to *p*-amino cinnamic acid with no reduction of the olefin bond. No selectivity is reported for dinitrobenzene as the diaminobenzene formation was observed.

Magnetically recoverable and recyclable Co–Co_2B nanocomposites described earlier from our laboratory for the catalytic and chemoselective reduction of nitroarenes using sodium borohydride have also been demonstrated for reduction of nitro group using hydrazine hydrate.[15c] Halo, ester, benzyloxy, nitrile and aliphatic nitro functionalities remained intact while allyloxy group showed 92 % selectivity.

Transfer hydrogenation of aromatic nitro compounds by hydrazine to the corresponding anilines is catalyzed by $(Bu_4N)[Ni(toluene\text{-}3,4\text{-}dithioalate)_2]$ in refluxing THF.[73] Nitroarenes with electron withdrawing groups are more easily reduced than with electron donating groups. In most cases aniline are the sole products while in few cases N-phenylhydroxyl amines are formed as intermediates and chief products at lower catalyst loading or shorter reaction times.

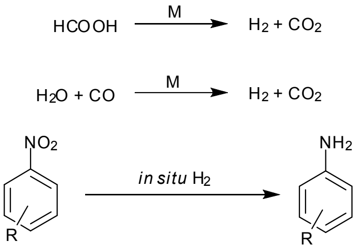
Commercial MoS_2 was found to be a highly selective catalyst for the reduction of nitrobenzenes to the corresponding anilines with hydrazine under mild conditions by Huang et al.[74] Very high selectivity is observed in the reduction of halonitrobenzenes and styrylnitrocompounds. Polyvinylpyrrolidine stabilized Ni or Co NPs were used for selective reduction of nitroarenes in presence of Cl, Br, I, CN. Aliphatic nitro compounds were also reduced in this system.[75a] Quantitative conversion of nitroarenes to anilines was obtained with cobalt modified Mo carbide supported on activated carbon in refluxing hydrazine hydrate. Sensitive reducible group like Cl, ester, aldehyde were tolerated during reduction.[75b] Reduction of nitroaromatics to anilines by hydrazine is also studied using carbon or graphite as catalysts.[75c]

Multiwalled carbon nanotubes were functionalized with small organic molecules containing specific ketonic carbonyl groups through noncovalent van der Waals and π–π interactions and utilized as metal free catalysts for reduction of nitroarenes.[76a] Boron doped pyrolytic graphene oxide were synthesized and explored for efficient reduction of nitrobenzene to aniline.[76b] However selectivity studies with this catalytic system is not undertaken. Reduced graphine oxide is also explored as catalyst for hydrogenation of nitrobenzene.[76c]

Hydrazine hydrate mediated reductions are much cleaner than the hydride processes as the by product is nitrogen and hydrogen. However selectivity in presence of the carbon-carbon double bond, triple bond and aldehyde may be difficult though has been claimed in some instances.

5. *In situ* hydrogen generation

Decomposition of formic acid or its salts leads to evolution of CO_2 gas along with H_2, leaving no residual wastes. Also CO-H_2O mixture commonly known as water gas in presence of metal support gives CO_2 and H_2. This molecular H_2 evolved is used for reduction, here are some recent examples exploiting this technique for nitroarene reduction.



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Scheme 7: Reduction of nitroarenes by transfer hydrogenation

Table 5: Reduction methodologies using transfer hydrogenation

Entry	Reagents (equiv.)	Solvent/conditions	Ref.
1	HCOOH (excess)	HTP water, 300 °C	77
2	CeY zeolite, HCOOH or $HCOONH_4$ (1.6)	MW, 140 °C	78
3	$Mo_3S_4H_3(dmpe)_3BPh_4$, HCOOH (3.5), Et_3N	THF, 70 °C	79
4	Au-TiO_2, CO (5 atm)	EtOH-H_2O, r.t.	80
5	Ru-MgF_2, CO (20 atm)	EtOH-H_2O, 175 °C	81
6	10 % Pd/C, NaH_2PO_2(5)	H_2O, 50 °C	82
7	5 % Pd/C, H_3PO_2 (1), NaH_2PO_2 (3)	ultrasound	83
8	H_3PO_3 (4)/H_3PO_2, NaI, aq. HBr	AcOH, 115 °C	84

Continuous hydrogenation of nitrobenzene to aniline is developed by Poliakoff and co workers in High Temperature-Pressurized Water (HTPW) using H_2 generated by thermal decomposition of HCOOH.[77] This reaction is carried out in absence of any added catalyst and can be conveniently performed on laboratory scale.

CeY Zeolite and formic acid under MW gave good yields of reduction products within 10 min. Aliphatic nitro compounds even with ester functionality were reduced to corresponding amines, while aldehyde, acid, amides, CN, Cl, Br were retained in corresponding anilines.[78]

Cubane-type $[Mo_3S_4X_3(dmpe)_3]^+$ clusters have been developed as catalysts (X=H) or precatalysts (X=Cl) for the reduction of functionalized nitroarenes using formates as a reducing agent.[79] Functional groups like nitrile, olefin, ketone, ester, amides and even aldehydes remained intact during reduction of nitro group.

Ru and Ir catalysts, which are not particularly selective under the conditions of conventional hydrogenation carried out with molecular hydrogen, when used in the Aqueous-Phase Reforming/Hydrogenation (APR/Hyd) process, become >99.9 % selective for hydrogenation of *o*-CNB to *o*-chloraniline.[80,81]

$$H_2PO_2^{\ominus} + 3OH^{\ominus} \longrightarrow HPO_3^{2\ominus} + 2H_2O + 2e^{\ominus}$$

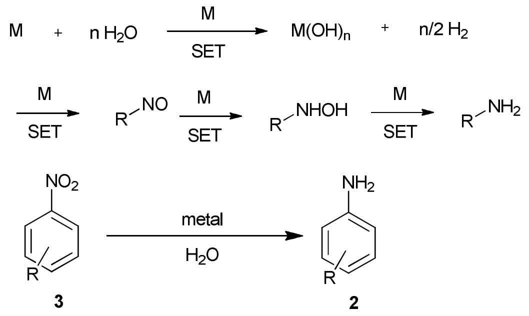
Hypophosphite are reducing agents as they get oxidized to phosphonates as shown above.[82a] Sodium hypophosphite is used as hydrogen source in water (containing 1 w/w% Tween 20) for reduction of nitro compounds by Oba et al.[82b] This process was catalyzed by Pd/C (10 mol%). Aromatic as well as aliphatic nitro compounds were reduced to amines at 50 °C in more than 99 % yields. Sodium hypophosphite is also used for dehalogenation, debenzylation and double bond hydrogenation. Similarly, mixture of phosphinic acid and sodium hypophosphite with Pd/C is used as heterogeneous catalyst in water: 2-methylTHF system by Popowycz and coworkers.[83] Here aliphatic nitro group was selectively reduced in presence of indole or coumarin. Nitroarenes were reduced to corresponding anilines in presence of CN, ester, keto and halogen groups.

A novel iodide-catalyzed reduction method using hypophosphorous and/or phosphorus acids was developed by Wu et al. to reduce both diaryl ketones and nitroarenes chemoselectively in the presence of chloro and bromo substituent in high yields.[84] This efficient and practical method has been successfully applied to a large scale production of a potential anticancer agent, Lonafarnib.

Milder conditions and stoichiometric use of decomposing reagents and simplified work up procedures are required to make these methods popular.

6. Direct metal

Active metal can react with water to liberate hydrogen. This liberated hydrogen in presence of metal can bring out reduction of nitro group. Also, metal could directly reduce nitro group by electron-transfer reaction with water acting as proton source.



Scheme 8: Reduction of nitroarenes using metal

Table 6: Reduction methodologies using direct metal

Entry	Metal reagent(equiv.)	solvent	Ref.
1	Fe nm powder (3)	H_2O, 210 °C	85
2	Fe NPs (3)	H_2O, r.t.	86
3	FeS (5), NH_4Cl	MeOH, H_2O,	87

		reflux	
4	Te (3)	H_2O, 275 °C	88
5	Zn (7), NH_4Cl	H_2O, 80 °C	89
6	Zn, CO_2 (80atm)	H_2O, 80 °C	90
7	Zn, CO_2 (1 atm)	H_2O, r.t.	91
8	Zn, CO_2 (1 atm)	H_2O, ultrasound	92
9	$RuCl_2(PPh_3)_3$ (0.025), KOH (0.25), Zn (3.3)	H_2O, dioxane, 40 °C	93
10	Zn (7), SiO_2-PEG	H_2O, r.t. - reflux	94
11	Sm (2), AcOH	[BMIM][BF_4], r.t.	95
12	Mn (2.5), $CuCl_2$ (0.05)	THF, H_2O, r.t.	96
13	$NbCl_5$ (2), In (8)	THF, r.t.	97

Nanosized activated metallic iron powder is used as reducing agent by Wang et al. for reduction of nitroarenes to anilines in water at 210 °C (near critical water).[85] This method unlike Bechamp reduction, avoids use of strong acidic conditions and could sustain substituent like OMe, COMe, COOEt, F, Cl, Br, and I. This method could also reduce nitronaphthalene to naphthylamine but not aliphatic nitro compounds and nitrostyrenes. Ranu and coworkers[86] have achieved similarly highly selective reduction of nitroarenes using iron metal NPs in water at room temperature. During the reaction a change in shape of Fe NPs was observed. The easily reducible functional groups CHO, COMe, CO_2Me, COOH, $CONH_2$, CN, N_3, I, Br, Cl, F, SCN, *O*-benzyl, *O*-allyl, *O*-TBDMS, *N*-benzyl, *N*-allyl, styrenoid double and triple bonds were unaffected.

Reduction is achieved in refluxing MeOH-water mixture using FeS and ammonium chloride by Dessai et al.[87] Sensitive substituent like chloro, ester, *N*-benzyl were unreactive in this reduction and corresponding anilines were obtained in 56 to 81 % yields. Te metal is used as reducing agent for preparation of anilines from nitro aromatics in neat critical water at 275 °C by Wang et al.[88] Electron donating (Me) and electron withdrawing (MeCO, Cl) were well tolerated. However incase of Br and I derivative competitive dehalogenation takes place. Carboxylic acid group also undergoes decarboxylation. This process does not reduce aliphatic nitro and nitrostyrenes.

Chemoselective reduction of nitroarenes to anilines is reported using Zn and NH_4Cl in water at 80 °C by Tsukinoki and Tsuzuki.[89a] The functionalities like ester, amide and halogens were unaffected and sterically hindered 2,6-dimethylnitrobenzene was also reduced to corresponding anilines in 95 % yield. Similarly zinc powder in aqueous solutions of chelating ethers is used by Kumar and Lokanatha Rai.[89b] Other reducible groups like ester, chloro, amide, ketone and styryl remained unaffected. Interestingly aliphatic nitro functionality present on 2-nitrodihydroindole also could be reduced by this method. The donor ether acts as a ligand and also serves as a co-solvent with water being the proton source. Using commercially available designer surfactant TPGS-750-M along with Zn dust and NH_4Cl, this reaction took place under mild condition at r.t. and tolerated wide range of functionalities. Antiarrhythmic agent procainamide was synthesized in 83 % yield in two steps.[89c] With Zn-H_2O-CO_2 system, water acted as direct hydrogen donor in super critical CO_2 as solvent.[90] This method by H. Jiang and Y. Dong gave excellent yields of reduction product in presence of F, Cl, Br, I, acid and ketone functional groups.

Controlled reduction of nitroarenes to *N*-phenylhydroxylamine was achieved by Liu et al using Zn in CO_2/H_2O system.[91] 88 % Yield of N-phenyl hydroxylamine was obtained when 3 eq. of Zn were used in 0.1MPa CO_2 at 25 °C for 1.5 h. Using this stoichiometric conditions, dinitrobenzene was selectively reduced to *m*-nitro-*N*-phenylhydroxylamine in 99 % yield. Similarly Zinc in CO_2-water mixture with application of ultrasound gave excellent yields in just 60 min. Other reducible functional groups like CN, keto, Cl, Br were not affected in these methods.[92] Also alkynes, ketones, or nitro groups were chemo selectively reduced using $RuCl_2(Ph_3P)_3$ as catalyst and Zn/water as stoichiometric reductant by Plietker and coworkers.[93]

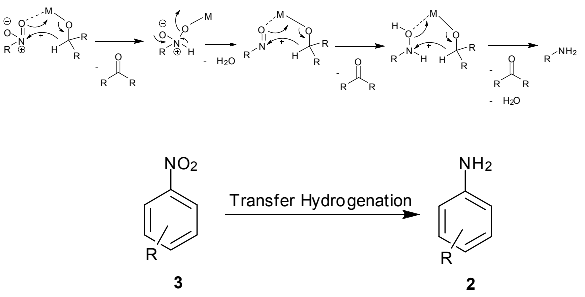
Reduction of nitro compounds to anilines is achieved in water using zinc powder and silica gel supported PEG by Reza et al.[94] The products were isolated in 68-92 % yield by mere acid base purification with retention of other substituent like NH_2, COOH, and also sensitive functionalities like CHO, Cl, CH_2Br.

Sm and AcOH in ionic liquid are used at r.t. for nitro-reduction in inert atmosphere by Zheng and Zhang.[95] In this system halogen, CHO, COOH, CN, NHTs groups were unaffected and corresponding anilines were obtained in 83 to 98 % yields.

Reduction of aromatic nitro compounds to anilines is reported in THF-water mixture at r.t. using Mn as reducing agent and $CuCl_2$ as catalyst by Sarmah and Dutta.[96] Nitro group was selectively reduced to NH_2 in presence of OH, NH_2, Cl, COOH, ester and CN with 75-88 % yield. The products were isolated in pure form by mere acid- base treatment. Similarly Yoo et al. have shown that $NbCl_5$/In system mediates an efficient and mild reduction of aromatic nitro compounds to the corresponding amines.[97] The Br, Cl, $COOCH_3$ and $COCH_3$ functionalities remained unaffected.

Metal reductions as such are very selective in reducing nitro functionality but stoichiometric requirement of metals make these processes unattractive.

7. MPV type redox processes using organic reducing agents (Transfer hydrogenation)



Scheme 9: Reduction of nitroarenes by non-classical reagents

Table 7: Reduction methodologies using non-classical reagents

Entry	Reagents (equiv)	Solvent/ conditions	Ref.
1	$LaFeO_3$, KOH (1), iPrOH	MW	98
2	Ru-acid activated montmorillonite clay or Ag-mesoporous poly-triallylamine, NaOH (2.5), iPrOH	80 °C	99
3	Polymer-bound palladium, K_3PO_4 (1.5), cyclohexanol	DMF, 110 °C	100
4	Ni-Fe_3O_4, KOH (2), glycerol	80 °C	101
5	(*2*-Pyridyl)phenyl-methanol (3.5)	toluene, 110 °C	102
6	Pinacol (4), $MoO_2Cl_2(dmf)_2$	toluene, MW, 150 °C	103
7	D-glucose (2), KOH (4)	H_2O:DMSO, 110 °C	104
8	Pd/C, 1,4-cyclohexadiene (6)	MeOH, MW, 120 °C	105a
9	$Pd_{13}Pb_9$ or $RhPb_2$	MeOH, Ar, 70 °C	105b

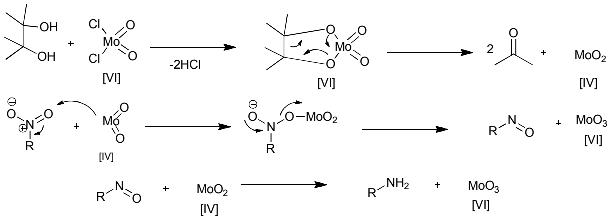
Perovskite-type $LaFeO_3$NPs were readily synthesized via thermal decomposition of the $La[Fe(CN)_6]·5H_2O$ complex by Farhadi and Siadatnas.[98] This nanosized perovskite-type oxide with an average particle size of 35 nm and a specific surface area 38.5 m^2/g was used as a reusable heterogeneous catalyst for selective reduction of aromatic nitro compounds into their corresponding amines by using propan-2-ol as the hydrogen donor under microwave irradiation. Chloro, bromo, nitro, ester, acid, ketone, nitrile and aldehyde group remained intact during this process. Transfer hydrogenation of nitroaromatics to anilines in isopropyl alcohol using KOH and Ru NPs stabilized on Montmorrilonite clay as catalyst is achieved by Sarmah and Dutta. Catalyst was selective towards nitro reduction to corresponding anilines without affecting F, Cl, Br or CN.[99a] Ag-mesoporous poly-triallyl amine catalyst is reported under similar conditions by Salam et al.[99b] Recently, Fe-SBA-15 hexagonal mesopores were efficiently used for reduction of different nitro substituted compounds using NaOH in refluxing isopropyl alcohol by Sanjini and Velmathi.[99c]

Polymer-bound palladium catalyst was prepared as PdO NPs bound on the surface of polystyrene beads by Min et al.[100] This catalytic system showed good activities in the reduction of nitroarenes and the hydrodehalogenation of aryl halides with 10 mol% PdO and K_3PO_4 (1.5 equiv.) in DMF/cyclohexanol at 110 °C.

Heterogeneous Fe_3O_4-Ni MNPs catalyst is demonstrated for hydrogen-transfer reactions by using the environmentally friendly solvent glycerol as a hydrogen donor by Gawande et al.[101]

(*2*-Pyridyl)phenyl methanol is used as hydrogen donor for reduction of aromatic nitro compounds to arylamines. These were subsequently subjected to conjugate addition through aza-Michael reaction in one pot manner.[102]

Pinacol is used as reducing agent in presence of $MoO_2Cl_2(dmf)_2$ as catalyst for reduction of nitro aromatics to anilines.[103] This reduction system was compatible with most halogens, amide, ester, nitriles, olefins, nitro, benzyl ether, thioether, pyridine ring and ketones. Good yields were obtained under MW condition and acetone and water are the only by-products in this reduction. This system could also be used for deoxygenating sulphoxides.



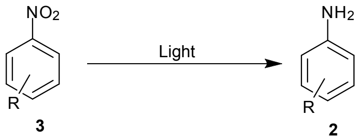
D-glucose, abundantly available carbohydrate is reported by Kumar et al. as a source of hydrogen for reduction of nitroarenes in catalyst free aqueous system.[104] D-glucose/KOH system in water: DMSO mixture is employed for this reduction of nitro arenes at 110 °C. Substituent like C≡N, CHO, C=C, C=N and halogens on nitroarenes were tolerated. Even dinitroarenes were found to selectively reduce to mononitroanilines in excellent yields.

Quinn et al. have shown that commonly available Pd/C or Pt/C catalyst is extremely effective with 1,4-cyclohexadiene as the hydrogen transfer source.[105a] For substrates containing potentially labile aromatic halogens, Pt/C is effective and results in little or no dehalogenation. In general, the reactions were complete within 5 min at 120 °C under microwave heating conditions. Furukawa and coworkers have used Pd and Rh based intermetallic catalysts for chemoselective catalytic transfer hydrogenation to nitro group in styrenes, stilbenes and indoles using MeOH and 4-methylcyclohexene as hydrogen donors.[105b]

Transfer hydrogenations using sustainable materials under mild conditions may go a long way in meeting the future demand of such reduction processes.

8. Light induced photo catalysis

Light induced activation of catalysts has helped in reducing the energy barrier for many reactions thus providing methods with mild conditions. Following are some reports describing the activation of passive catalysts in presence of reducing agents to facilitate the reduction under mild conditions.



Scheme 10: Reduction of nitroarenes

Table 8: Reduction methodologies using light sources

Entry	reagents	Solvent/ conditions	Ref.
1	TiO_2, Hg arc(>300 nm), oxalic acid,	H_2O-MeCN, r.t.	106
2	Ru-dye-TiO_2, TEOA, 530 nm	MeCN, r.t.	107
3	TiO_2, oxalic acid/formic acid, HCl, UV	H_2O, r.t.	108
4	CdS nanosphere / reduced graphene oxide, 420 nm, $HCOONH_4$	H_2O, r.t.	109
5	CdS, nanowires, reduced graphene oxide, >420 nm, $HCOONH_4$	H_2O, r.t.	110
6	$HCOONH_4$, Pd@CeO_2, <420 nm	H_2O, r.t.	111
7	$PbBiO_2Br$, 440 nm, TEOA	MeCN, r.t.	112

TiO_2 is used as photocatalyst under UV irradiation for reduction of nitrobenzene to aniline using oxalic acid as reducing agent and hole scavenger by Kominami and coworkers.[106] Vinyl, halogens, acid and ketones were unreactive in this reduction.

Ru dye sensitized TiO_2 is reported by Konig and coworkers as catalyst in presence of green light for this reduction and triethanolamine (TEOA) as reducing agent.[107a] Addition of small amount of transition metals (less than 0.1 mol%) led to significant enhancement of photocatalytic activity. The optimal catalytic amount of the transition metal (Pt, Pd, Au and Ag) required for quantitative reduction depended on the nature of the metal and the method of preparation. Amounts higher than 1 mol% decreased the catalytic activity. The photocatalytic activity also depended upon the oxidation state of the metal source. Critical cluster sizes of 2 nm are required for good photocatalytic activity and the size depended upon the metal loading. Similar morphologies were found for all the transition metals. A quantum efficiency of 8% was determined for the reduction reaction under the optimized reaction conditions. Aldehyde, ketone, ester, cyano and halogen were compatible for this reduction. Dehalogenation occurs with higher loading of platinum. Green light photoreduction of nitrobenzene was also demonstrated on a laboratory preparative scale. Chen et al.[107b] have reported reduction of nitro compounds using TiO_2 photocatalyst by UV and Vis dye-sensitized systems.

Kominami and coworkers[108] examined photocatalytic reduction in aqueous suspensions of titanium(*IV*) oxide (TiO_2) in the presence of hole scavengers under various conditions. *m*-Nitrobenzenesulfonic acid was almost quantitatively converted into *m*-aminobenzenesulfonic acid in the presence of formic acid as a hole scavenger under deaerated conditions with high efficiency (>99 %). Other nitroaromatic compounds were photocatalytically reduced into the corresponding amines using same catalyst and oxalic acid. Xu and coworkers[109] reported self-assembly of uniform CdS nanospheres/ graphene (CdS NSPs/GR) hybrid nanocomposites via electrostatic interaction of positively charged CdS nanospheres (CdS NSPs) with negatively charged graphene oxide (GO), followed by GO reduction via a hydrothermal treatment. These nanocomposites exhibited high visible light photocatalytic performance and excellent reusability toward selective reduction of aromatic nitro organics to corresponding amino organics in water in presence of ammonium formate as hole quencher. 2-Nitrophenol, 4-nitrophenol, 2-nitroaniline, 1-chloro-4-nitrobenzene, 4-nitroanisole and 1-bromo-4-nitrobenzene were successfully reduced to their amines without affecting the other groups present on benzene ring. As during reduction graphene and CdS are not affected, the catalyst system can be potentially recycled. Similarly, the CdS nanowires–reduced graphene oxide nanocomposites (CdS NWs–RGO NCs) were synthesized by same process in the same laboratory. Furthermore, the presence of RGO also improves the adsorption capacity of CdS NWs– RGO NCs toward aromatic nitro organics.[110]

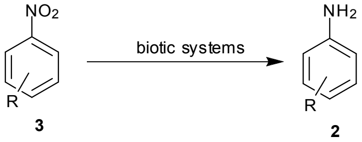
Pd NP cores encapsulated within CeO_2 hollow shells are used for thermocatalytic and photocatalytic reduction of aromatic nitro compounds to anilines in water at room temp by Zhang and Xu.[111] Thermocatalytic method uses $NaBH_4$ as reducing agent whereas photocatalytic method uses ammonium oxalate as reducing agent and visible light irradiation. This catalyst showed good selectivity for nitro reduction in presence of Cl and Br.

$PbBiO_2Cl$ and $PbBiO_2Br$ were used as catalyst for reduction of nitrobenzene derivatives using TEOA in blue light by Konig's group.[112] Catalysts were selective for nitro reduction in presence of CN, CHO, keto but could reduce pyridinealdehyde. The catalyst could be reused many times after sonication to remove the passivity.

Direct sunlight mediated photochemical reductions on a large scale particularly for environmental cleaning will be of great help in future.

9. Biotic reduction

Although reduction of nitroarenes was considered as a synthetic process so far, following are some of the reports that indicate the transformation of nitroarene to anilines as a part of biological processes.



Scheme 11: Reduction of nitroarenes

Table 9: Reduction methodologies using natural sources

Entry	Natural sources	conditions	Ref.
1	*Escherichia coli reductases*	pH 7 buffer, 30 °C	113
2	Plant cells from *Lens culinaris* seeds	H_2O, 30 °C	114
3	Plant cells from Grapes *(Vitis vinifera* L.)	H_2O, 25 °C	115
4	Cattle tick *Boophilus microplus*, Spider *Nephila plumipes*	*in vivo*	116
5	Microbial consortium,	H_2, pH 6.5-6.8, 30 °C	117
6	Biocatalysed cathode	Glucose, 25 °C	118
7	FMN-dependent nitro-reductase	Glucose	119
8	BaNTR1, BmGDH NADP	Glucose, 0.1 M sodium phosphate buffer, 30 °C	120

Mercier et al. observed that *Escherichia coli* is able to reduce azo compounds such as methyl red (MR) and nitro compounds such as 7-nitrocoumarin-3-carboxylic acid (7NCCA).In depth study revealed enzyme AzoR to reduce both MR and 7NCCA, whereas enzymes NfsA and NfsB could only reduce the nitro compound.[113] Similarly, a series of aliphatic and aromatic aldehydes and ketones, as well as some nitrocompounds were reduced using whole plant cells from *Lens culinaris* seeds by Ferreira et al .[114]

Plant cells from a grape (*Vitis vinifera* L.) reducing aromatic nitro compounds under mild conditions to the corresponding hydroxylamines was observed by Li et al.[115]

Two species of Arachnida *Boophilis Microplus* (a cattle tick) and *Nephila Plumipes* (a Sydney spider) metabolized ^{14}C nitrobenzene to aniline *in vivo*. These species could also metabolise *N*,*N*-dimethylamino-azobenzene to anilines. This was the first and only report of observing reduction of nitrobenzene to aniline in living organisms by Holder and Willox.[116]

Conversion of nitrobenzene to aniline, a less toxic end product that can easily be mineralized was carried out in a continuous-flow anaerobic bioreactor using H_2 gas and a microbial consortium by Cao et al.[117] This reduction is sensitive to both pH and temperature. Optimum reduction was obtained in pH 6.5-6.8 and at 30 °C.

A fed-batch bioelectrochemical system with microbial catalyzed cathode could transform nitrobenzene to aniline within 24 h when a voltage of 0.5 V was applied in the presence of glucose was reported by Wang et al.[118]

FMN-dependent ene-reductases and nitroreductases can catalyze or mediate a diverse spectrum of chemical reactions due to the chemical versatility of the flavin cofactor. Nitroreductases have evolved as natural remediation tools in contaminated environments with a major role in the reduction of toxic nitro-aromatics.[119]

Bacterial nitroreductase BaNTR1 is recently identified and used as biocatalyst by Xu and coworkers for controllable reduction of nitroarenes with electron withdrawing groups like NO_2, CN, amide, acid and ester to corresponding *N*-aryl hydroxylamines.[120]

Enzymatic reductions have shown a great promise and sustained research in this field is required for future developments.

Conclusions

The area of research comprising methods for reduction of nitroarenes continues to attract synthetic chemist due to problems associated with selectivity, cost of process, ease of reaction and the benigness involved. The market potential for a new industrial application is also very high due to the demand of the final reduction product aniline. With the rapidly developing nanotechnology new and newer materials are getting generated and this newly generated nano materials may lead to more selective and more efficient processes. Of the newly tried metals gold has shown a great promise and it may be a choice metal replacing traditional palladium and platinum metal. Further progress in this field is expected particularly using magnetic nano composites, which can be recycled easily. Research in non coinage metals will continue to take place due to the cost factor involved in the noble metal reduction processes. Cost effective green alternative transfer hydrogen, enzymatic and photochemical reductions methods are the ones, where more progress is expected.

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