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Efficient Reduction of Nitroarenes over Nickel-Iron Mixed Oxide Catalyst Prepared from a Nickel-Iron Hydrotalcite Precursor

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Abstract: Nickel-iron mixed oxide prepared from a nickel-iron hydrotalcite precursor was found to be a highly efficient catalyst for the chemoselective reduction of nitroarenes under mild reaction conditions.

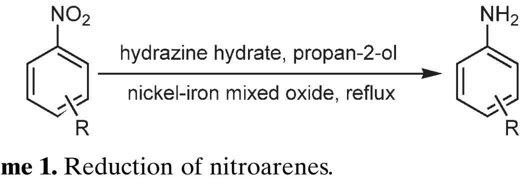
Keywords: aromatic amines; chemoselectivity; hydrogen transfer; hydrotalcites; nitroarenes; reduction

Aromatic amines are an important class of compounds frequently used as key intermediates in the synthesis of pharmaceutical products, dyestuffs and polymers. Various methods have been reported for the preparation of aromatic amines from the corresponding aromatic nitro compounds. Compared to the generally used methods[1] that need either strong acid medium, which corrodes the reaction equipment seriously, or hazardous molecular hydrogen and high-pressure reactors, catalytic transfer hydrogenation, as a safer and greener way, has attracted more and more attention.[2] Hydrazine hydrate is widely employed as hydrogen donor in catalytic transfer hydrogenation because the hydrazine reduction produces harmless by-products such as nitrogen gas and water. The usual catalysts used in the hydrazine reduction of nitroarenes are zinc,[3] magnesium,[4] $FeCl_3 \cdot 6\,H_2O$-activated carbon,[5] iron(III) oxide[6] and iron oxide hydroxide.[7] Recently magnesium-iron mixed oxide prepared from a magnesium-iron hydrotalcite-like precursor has also been reported as an effective catalyst for the hydrazine reduction of aromatic nitro compounds.[8]

Hydrotalcite-like compounds belong to the anionic clay materials and have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot m\,H_2O$ (where M is a metal and A is an anion).[9] Thermal decomposition of hydrotalcite-like compounds can form highly thermally stable and highly dispersed mixed oxides with large surface area and obvious basic properties, as well as redox properties if a reducible metal is contained in the network. In recent years, mixed oxides prepared from hydrotalcite-like precursors have received increasing interest because these oxides often display good activity and selectivity in various reactions.[10] Nickel-iron hydrotalcite, a very important member of the hydrotalcite family, has been widely researched[11] and applied as adsorbent[12] and catalyst[13] over the past decade. However, it is surprising that, until now, there are few reports about the application of nickel-iron mixed oxide obtained from a nickel-iron hydrotalcite precursor as catalyst in the organic synthesis.[14]

In continuation of our interest in exploring the applications of mixed oxides prepared from hydrotalcite-like precursors in reduction, herein, we report for the first time the use of nickel-iron mixed oxide from a nickel-iron hydrotalcite-like precursor as catalyst in the reduction of nitroarenes to prepare aromatic amines (Scheme 1). We expect that the present study could play a role of a 'catalyst' which will accelerate the investigation of nickel-iron mixed oxide as a catalyst in organic synthesis.

As shown in Table 1, various nitroarenes with different substituted groups have been successfully reduced over nickel-iron mixed oxide catalyst. Reduction of 2-chloronitrobenzene (entry 1) and 1,2-dichloro-4-nitrobenzene (entry 2), respectively, gave the corresponding amines in almost quantitative yields (97% for entry 1 and 98% for entry 2) and the dehalogenation, which often occurs in the catalytic hydrogenation of nitroarenes bearing a halide group,[15] was successfully avoided under the reaction conditions. The chemoselective reduction was also observed in the case of 4-nitrobenzoic acid ethyl ester (entry 3), where the reducible ester group remained intact. Moreover, reduction of nitroarenes bearing other



Scheme 1. Reduction of nitroarenes.

Table 1. Reduction of nitroarenes using hydrazine hydrate over nickel-iron mixed oxide catalyst prepared from a nickel-iron hydrotalcite-like precursor.[a]

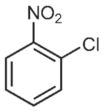
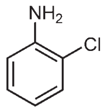
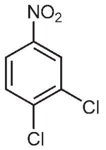
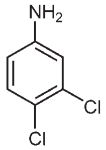
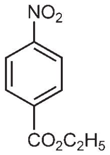
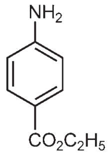
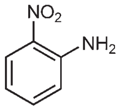
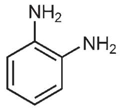
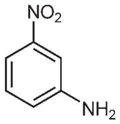
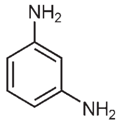
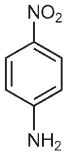
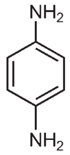
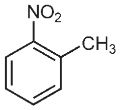
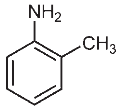
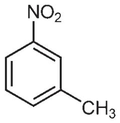
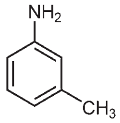
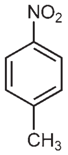
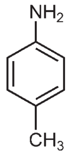
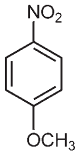
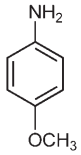
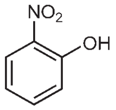
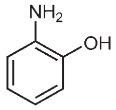
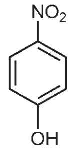
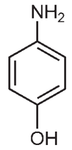
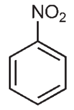
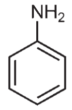
Entry	Substrate	Time [min]	Product[b]	Yield [%][c]
1		61		97
2		25		98
3		29		94
4		112		98
5		109		99
6		142		97
7		116		99
8		98		99
9		94		94
10		90		98
11		51		90

Table 1. (Continued)

Entry	Substrate	Time [min]	Product[b]	Yield [%][c]
12		105		93
13		89		96

[a] *Reaction conditions:* 0.5 g of aromatic nitro compound, 1 mL hydrazine hydrate, 0.15 g nickel-iron mixed oxide, 15 mL propan-2-ol, reflux.

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

[c] Isolated yields were based on a single experiment and were not optimized.

functional groups such as amide, methyl, methoxy and hydroxy was also carried out to investigate the scope of our catalytic system. It was found that all the reactions (entries 4–12) proceeded very smoothly (yields: 90–99%) and that these functional groups were compatible with the present system. In addition, in all cases (entries 1–13), the azoxy, azo and hydrazo compounds, as the usual side products of reduction of nitroarenes under basic conditions, were not observed in the final reaction system.

For the purpose of checking the reusability of the nickel-iron mixed oxide catalyst, consecutive cycles were executed and the results, summarized in Table 2, showed that the yield was unaffected during up to three cycles.

To further broaden the scope of this study, the present catalytic system had been extended towards the reduction of sulphur-containing aromatic nitro compounds. The sulphur-containing aromatic amines as important pharmaceutical intermediates have been widely produced. However, owing to the presence of

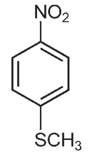
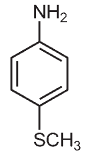
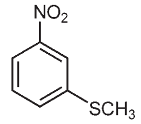
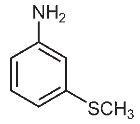
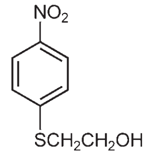
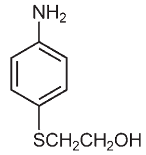
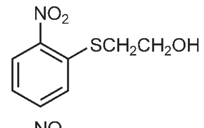
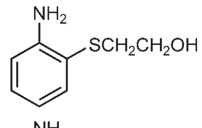
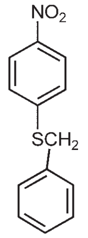
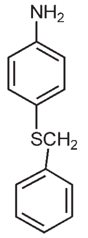
Table 2. Reusability of the nickel-iron mixed oxide catalyst prepared from a nickel-iron hydrotalcite-like precursor for 1,2-dichloro-4-nitrobenzene reduction.[a]

Recycling Times	Time [min]	Yield [%][b]
1	25	98
2	25	97
3	28	97

[a] Reaction conditions: 0.5 g of 1,2-dichloro-4-nitrobenzene, 1 mL hydrazine hydrate, 0.15 g nickel-iron mixed oxide, 15 mL propan-2-ol, reflux.

[b] Isolated yields.

Table 3. Reduction of sulphur-containing nitroarenes using hydrazine hydrate over nickel-iron mixed oxide catalyst prepared from a nickel-iron hydrotalcite-like precursor.[a]

Entry	Substrate	Time [min]	Product[b]	Yield [%][c]
1		40		96 (10[d])
2		66		96
3		46		98
4		28		94
5		31		97

[a] Reaction conditions were the same as those of Table 1.

[b] The identity of all the products was established by ^{1}H NMR spectra and MS.

[c] Isolated yields were based on a single experiment and were not optimized.

[d] Reported by Maleczka et al. Conditions used by them: 1 mmol of substrate, 5 mol% of $Pd(OAc)_2$, 4 equivs. of PMHS, 2 equivs. of KF, 2 mL of degassed H_2O, 5 mL of THF, room temperature, 30 min.

a sulphur atom which may poison the metal used as catalytic hydrogenation catalyst, at present, the methods employed generally in industry are sulphide reduction[16] and Fe/HCl reduction.[17] It is well known that these two methods are very hazardous to the environment due to the release of waste water containing sulphur moieties and iron sludges. Therefore, finding an eco-friendly way for preparing sulphur-containing aromatic amines is an especially urgent subject from the industrial point of view. Here, we report our results in this area. From Table 3 we can see that nickel-iron mixed oxide successfully catalyzed the reduction of sulphur-containing nitroarenes and the yields were good to excellent (94–98%). Furthermore, in the case of 1-methylthio-4-nitrobenzene (entry 1), an interesting comparison between our results with that reported by Maleczka et al.[18] has also been performed. Under our reaction conditions, the 4-methylthiobenzeneamine as the only product was obtained in almost quantitative yield (96%). In contrast, Maleczka's method gave a complex mixture including only approximately 10% yield of the expected amine. The low yield had been attributed to the negative effect of sulphur on palladium by Maleczka et al.

Control experiments were performed using 4-nitrotoluene according to the general procedure, but without the use of nickel-iron metal oxide or in the absence of hydrazine hydrate. The reactions did not produce any desired product. This clearly showed that both nickel-iron metal oxide and hydrazine hydrate played important roles for the reduction of nitroarenes in our reaction system.

Although a detailed research about the reaction mechanism has not been undertaken, a proposed mechanism is shown in Scheme 2, which is based on the available literature[3,8b,19] and the following facts: (1) hydrazine hydrate is a known two-electron reducing agent;[20] (2) in our certain cases, nitroso and/or

$$2Fe^{3+} + N_2H_4 \longrightarrow 2Fe^{2+} + 2H^+ + N_2H_2$$

$$2Fe^{3+} + N_2H_2 \longrightarrow 2Fe^{2+} + 2H^+ + N_2$$

$$ArNO_2 \xrightarrow[2H^+]{2e^-} ArNO \xrightarrow[2H^+]{2e^-} ArNHOH \xrightarrow[2H^+]{2e^-} ArNH_2$$

Scheme 2. Proposed reaction mechanisms.

hydroxylamine intermediates have been successfully detected by HPLC at the initial stage of reaction; (3) nickel-aluminium or nickel-magnesium-aluminium mixed oxides prepared from the corresponding hydrotalcite-like precursors can not catalyze the reduction of nitroarenes under similar reaction conditions.

In conclusion, we have developed an exceedingly efficient and highly chemoselective approach to prepare aromatic amines from the corresponding aromatic nitro compounds using hydrazine hydrate over nickel-iron mixed oxide obtained by calcinations of nickel-iron hydrotalcite-like precursor. This method is simple and environmentally friendly. The present study opens up the application of nickel-iron mixed oxide as catalyst in the field of reduction of nitroarenes. In addition, since nickel-iron mixed oxide has shown excellent activity for the reduction of sulphur-containing aromatic nitro compounds, we believe that the catalytic system described here may be a promising alternative to the sulphide reduction and Fe/HCl reduction which are widely used for preparing sulphur-containing aromatic amines at present in industry. Further studies to optimize reaction conditions and explore the application of nickel-iron mixed oxide as catalyst in other reduction reactions are in progress in our laboratory.

Experimental Section

Preparation of Nickel-Iron Mixed Oxide Catalyst

Nickel-iron mixed oxide was prepared following the method described by Rives et al.[11a] An aqueous solution (100 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (10 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (6.94 g) with an Ni/Fe molar ratio of 2 was added dropwise into 100 mL of 1.17 mol/L NaOH and 0.34 mol/L Na_2CO_3 solution at room temperature under vigorous mechanical stirring. After the addition, the suspension was stirred for 2 h. Then the mixture was heated to 50 °C and maintained at this temperature for 2 days. The solid formed was filtered, washed with deionized water and dried at 50 °C for 12 h. Afterwards, the dried product, which showed a typical hydrotalcite-like pattern by XRD (Rigaku D/Max 2400, CuKα), was heated at 450 °C in air for 3 h and then cooled to the room temperature under a nitrogen atmosphere to obtain the nickel-iron mixed oxide catalyst. The XRD of catalyst obtained showed the formation of NiO phase only.

Preparation of Nickel-Aluminium and Nickel-Magnesium-Aluminium Mixed Oxide Catalysts

Nickel-aluminium and nickel-magnesium-aluminium mixed oxides were respectively prepared following the methods described in detail by Choudary et al.[21] and Obalová et al.[22] and characterized by XRD.

General Experimental Procedure for the Reduction of Nitroarenes

A mixture of aromatic nitro compound (0.5 g), propan-2-ol (15 mL) and fresh prepared nickel-iron mixed oxide catalyst (0.15 g) was heated to reflux. Then hydrazine hydrate (1 mL) was added dropwise and the reaction mixture was stirred under reflux for several minutes. After completion of the reduction (monitored by TLC), the reaction mixture was filtered and the catalyst was washed thoroughly with methanol. Then the filtrate was concentrated under vacuum. The residue was loaded on a silica gel column and eluted with *n*-hexane and ethyl acetate to afford the product. All the products were characterized by ^1H NMR (Varian INOVA 400M with TMS as an internal standard) and MS (HP 6890GC/5973 MSD or HP 1100 LC-MSD). For recycling purposes, at the end of the reaction the catalyst was recovered by simple filtration and washed completely with methanol. Then it was dried under reduced pressure and reused for the subsequent cycles.

Acknowledgements

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