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Preparation of Copper Nanoparticles and Catalytic Properties for the Reduction of Aromatic Nitro Compounds

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A novel copper nanoparticles were synthesized from cupric sulfate using hydrazine as reducing reagents. A series of aromatic nitro compounds were reacted with sodium borohydride in the presence of the copper nanoparticles catalysts to afford the aromatic amino compounds in high yields. Additionally, the catalysts system can be recycled and maintain a high catalytic effect in the reduction of aromatic nitro compounds.

Key Words : Copper, Nanoparticles, Catalysis, Nitro reduction, Aromatic amino compounds

Introduction

Aromatic amino derivatives are pivotal intermediates for the synthesis of biologically and pharmaceutically active molecules. A number of amino aryl compounds have shown their wide application in dyes, pharmaceuticals, rubber, synthetic resins, paints, plastics and other industries in recent years.[1] In general, the amino aryl compounds can be obtained by the reduction of the nitro aryl compounds. There are several approaches to realize the reduction process: metal/acid reduction,[2,3] catalytic hydrogenation,[4-6] electrolytic reduction,[7] homogeneous catalytic transfer hydrogenation,[8] heterogeneous catalytic transfer hydrogenation,[9-13] *etc.* However, these methods have certain shortcomings:[14] metal/acid system has poor selectivity and acid brings severe corrosion to the equipment; catalytic hydrogenation employs a higher reaction pressure which may bring great danger; homogeneous or heterogeneous catalytic transfer hydrogenation could perform well only in the existence of expensive metals such as palladium, platinum, ruthenium *etc*., and separation of the target product is difficult. In the past decades, substances containing copper, as an important organic reaction catalyst, have been given much attention by materials scientists and chemists.[15-20] Furthermore, the excellent catalytic efficiency of copper nanostructure made it become a research focus at present both in preparation and application in organic synthesis. Copper has a low price, low toxicity, and copper nanostructure can be recycled to reduce the cost. Here, we report the preparation of copper nanoparticles (Cu NPs), which can effectively reduce aromatic nitro compounds to aromatic amino compounds in the presence of tetrahydrofuran (THF)/H_2O and sodium borohydride ($NaBH_4$).

Experimental

General. Unless otherwise stated, all reactions were carried out without taking precautions to exclude air and moisture. All solvents were used as received. All the chemicals were purchased from commercial sources and used as received unless stated otherwise. All reaction temperatures refer to bath temperatures. Column chromatography was carried out on silica gel (200-300 mesh). NMR spectra were recorded on a Bruker 400 MHz spectrometer. The X-ray diffraction (XRD) patterns were recorded on Germany Bruker AX in the range of 5-80°. TEM images were carried out using a Philips CM10 transmission electron microscope.

Preparation of Cu NPs. 5 mL $CuSO_4$(0.1 M) and 10 mL dodecyl benzene sulfonic acid sodium (DBS) (0.5 M) solution were taken into 210 mL deionized water in a three-necked flask equipped with a spherical condenser. 30 mL hydrazine (0.5 M) solution was then added dropwise to the above solution when the reaction mixture was heated to 100 °C under constant severe stirring. The reaction solution was refluxed for 40 min. After the completion of reaction and allowing the mixture to cool to room temperature, the reaction liquid was separated using a hydroextractor at 3500 rpm for 30min, washed three times with water and ethanol, after that dried it at 60 °C for 5 h in a vacuum dryer.

General Procedure for the Reduction of Nitro Aryl Compounds. A mixture of nitrobenzene (1 mmol), copper nanoparticles (0.1 mmol) and THF/H_2O (v/v = 1:2) were added into a three-necked flask, and 3 mmol sodium borohydride which were dissolved in 5 mL distilled water were then added dropwise to the above solution under the continuous stirring. The mixture was stirred at 50 °C and monitored by TLC. After the completion of the reaction, allowing the mixture to cool to room temperature and filtered. The filtrate was washed with methylene chloride, the organic layer was washed successively with brine and water, then dried with anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give desired product.

Aniline (Table 1, entry 7): R_f = 0.47 (Petroleum ether: Ethyl acetate = 4:1); Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.54 (d, 2H), 6.6-6.63 (d, 2H), 6.71-6.75 (s, 1H), 7.11-7.14 (d, 2H).

4-Toluidine (Table 3, entry 1): R_f = 0.59 (Petroleum ether:Ethyl acetate = 4:1); mp 43-45 °C; ^{1}H NMR ($CDCl_3$,

400 MHz) δ 2.23 (t, 3H), 3.49 (d, 2H), 6.59-6.61 (d, 2H), 6.958-6.97 (d, 2H).

4-Chloroaniline (Table 3, entry 2): R_f = 0.44 (Petroleum ether:Ethyl acetate = 4:1); mp 71-72 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (d, 2H), 6.59-6.62 (d, 2H), 7.09-7.11 (d, 2H).

3-Chloroaniline (Table 3, entry 3): R_f = 0.50 (Petroleum ether:Ethyl acetate = 4:1); Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.66 (s, 2H), 6.46 (d, 1H), 6.59 (s, 1H), 6.69 (d, 1H), 7.01 (t, 1H).

4-Aminophenol (Table 3, entry 4): R_f = 0.53 (Petroleum ether:Ethyl acetate = 4:1); mp 187-191°C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.41 (d, 2H), 6.39-6.42 (d, 2H), 6.45-6.48 (d, 2H), 8.32 (s, 1H).

4-Anisidine (Table 3, entry 5): R_f = 0.23 (Petroleum ether:Ethyl acetate = 4:1); mp 57-58 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.05-3.62 (d, 2H), 3.745 (t, 3H), 6.64-6.67(d, 2H), 6.74-6.76 (d, 2H).

4-Aminobenzyl Alcohol (Table 3, entry 6): R_f = 0.25 (Petroleum ether:Ethyl acetate = 1:1); mp 58-60 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65-1.67 (s, 1H), 3.64-3.78 (d, 2H), 4.53 (d, 2H), 6.6-6.68 (d, 2H), 7.13-7.26 (d, 2H).

Ethyl 4-Aminobenzoate (Table 3, entry 7): R_f = 0.30 (Petroleum ether:Ethyl acetate = 4:1); mp 86-88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34-1.38 (t, 3H), 4.01 (d, 2H), 4.29-4.35 (d, 2H), 6.34-6.66 (d, 2H), 7.85-7.87 (d, 2H).

1-Naphylamine (Table 3, entry 8): R_f = 0.65 (Petroleum ether:Ethyl acetate = 4:1); mp 46-47 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.0 (d, 2H), 6.7 (s, 1H), 7.2-7.28 (d, 2H), 7.38-7.42 (d, 2H), 7.73-7.78 (d, 2H).

***o*-Toluidine (Table 3, entry 9):** R_f = 0.44 (Petroleum ether: Ethyl acetate = 8:1); Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (t, 3H), 3.53 (d, 2H), 6.65-6.72 (d, 2H), 7.01-7.05 (d, 2H).

***m*-Toluidine (Table 3, entry 10):** R_f = 0.44 (Petroleum ether:Ethyl acetate = 4:1); Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (t, 3H), 3.51 (d, 2H), 6.46-6.49 (d, 2H), 6.56-6.58 (s, 1H), 7.01-7.05 (s, 1H).

4-Ethylaniline (Table 3, entry 11): R_f = 0.55 (Petroleum ether:Ethyl acetate = 4:1); Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18-1.21 (t, 3H), 2.43-2.49 (d, 2H), 3.36 (d, 2H), 6.52-6.55 (d, 2H), 6.89-6.91 (d, 2H).

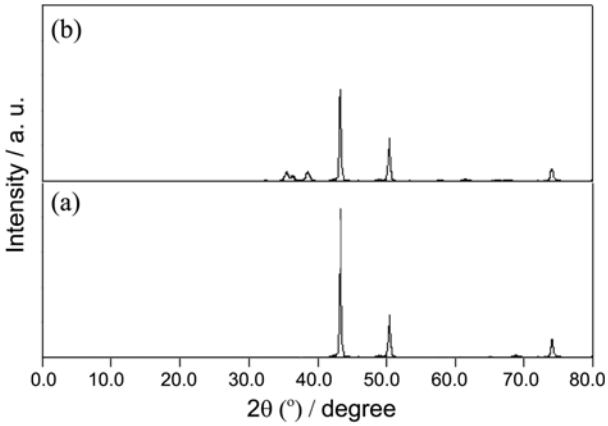


Figure 1. XRD patterns of (a) fresh Cu NPs and (b) reused Cu NPs.

Results and Discussion

The Cu NPs were characterized by XRD measurements. Figure 1(a) shows an XRD pattern of the Cu NPs. The reflections for Cu NPs are observed in XRD pattern at 2θ value of 43.3, 50.5 and 74.1, representing diffraction crystal surface [111], [200] and [220]. The peaks in our samples followed those in the standard material (JCPDS file no. 04-0836). After using one time, the catalyst's XRD curve is displayed in Figure1b. There are some new small peaks, which can be attributed to be partly oxidated of Cu NPs. It can also explain the slight decrease of aniline yield in the recyclable experiments.

TEM images of the Cu NPs are showed in Figure 2, in which each big spherical (about 100 nm) composed a lot of little particles. The size and shape of these nanoparticles are moderately uniform and dispersed well, no observing obvious agglomeration.

To identify optimum reaction conditions, the reduction reactions of nitrobenzene were first carried out in the absence or presence of different copper sourse catalysts at elevated temperatures. Selected results from our screening experiments are summarized in Table 1. Our studies showed that copper salt and copper NPs can catalysis the reduction reactions of nitrobenzene in the different degree (Table 1, entries 2-7), whereas without added copper source the reaction has been

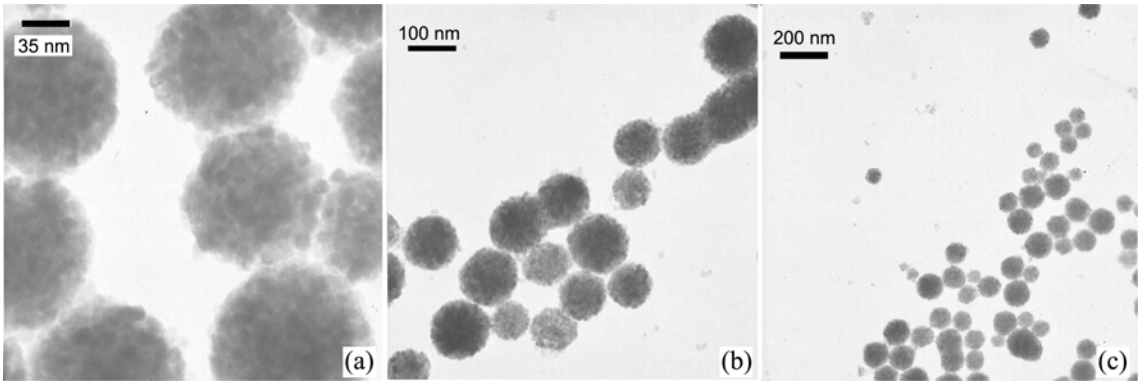
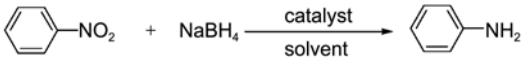


Figure 2. TEM images of Cu NPs.

Table 1. Reduction of nitrobenzene under different conditions[a]



Entry	Catalyst (mol %)	Solvent	Time (h)	T (°C)	Yield%[b]
1	-	THF/H_2O (1:2)	4	50	< 3
2	$CuSO_4$ (10.0)	THF/H_2O (1:2)	4	50	71
3	CuI (10.0)	THF/H_2O (1:2)	4	50	71
4	CuO (10.0)	THF/H_2O (1:2)	3	50	79
5	$CuCl_2$ (10.0)	THF/H_2O (1:2)	2	50	82
6	$Cu(OAC)_2$ (10.0)	THF/H_2O (1:2)	2	50	85
7	Cu NPs (10.0)	THF/H_2O (1:2)	2	50	98(95)
8[c]	Cu NPs (10.0)	THF/H_2O (1:2)	4	50	< 3
9	Cu NPs (10.0)	H_2O	4	50	66
10	Cu NPs (10.0)	DMF	4	50	77
11	Cu NPs (10.0)	CH_2Cl_2	4	50	76
12	Cu NPs (8.0)	THF/H_2O (1:2)	2	50	87
13	Cu NPs (5.0)	THF/H_2O (1:2)	2	50	77
14	Cu NPs (10.0)	THF/H_2O (1:2)	2	30	82
15	Cu NPs (10.0)	THF/H_2O (1:2)	2	40	90
16	Cu NPs (10.0)	THF/H_2O (1:2)	2	60	79
17	Cu NPs (10.0)	THF/H_2O (1:2)	2	70	78
18	Cu NPs (10.0)	THF/H_2O (1:2)	2	80	72
19	Cu NPs (10.0)	THF/H_2O (1:2)	2	90	77
20	Cu NPs (10.0)	THF/H_2O (1:2)	2	100	75

[a]Reaction conditions: nitrobenzene (1 mmol), $NaBH_4$ (3 equiv), Copper source (10 mol %), THF/H_2O (v/v = 1:2) (3 mL), Temp., Time. [b]GC yield. Isolated yield is in parenthesis. [c]$NH_2NH_2{\cdot}H_2O$ was used as the reductant for $NaBH_4$.

proven ineffective, no affording the desired product (Table 1, entry 1). Furthermore, in contrast to $NaBH_4$, a control reaction conducted in the presence of Cu NPs catalyst and using hydrazine as reducing reagents resulted in no conversions of starting materials (Table 1, entries 8). The reactions with different solvents (H_2O, DMF and CH_2Cl_2) occurred with moderate conversions (Table 1, entries 9-11). The loading scale of the Cu NPs catalyst (Table 1, entries 12 and 13) and the impact of reaction temperature (Table 1, entries 14 and 20) on this reaction were also assessed. Notably, the treatment of nitrobenzene with $NaBH_4$ (3 equiv) in the Cu NPs catalyst (10 mol %) along with THF/H_2O (v/v = 1/2) at 50 °C led to the desired aniline in 98% yield after 2 h (Table 1, entry 7). It should be noted that the reaction was carried out without exclusion of oxygen and moisture.

In order to investigate the recycling of the Cu NPs catalyst, the reduction of nitrobenzene in a scale of 10 mmol was tested under the optimum reaction conditions. After filtering off the catalyst, Cu NPs was washed with distilled water and ethanol, and then dried in a vacuum oven at 60 °C for 5 h. In the next reaction, we reused the dried catalyst directly. The same procedure was repeated for all further cycles. It should be noted that the Cu NPs catalyst was recycled for three times with no significant drop in reaction conversions (Table 2).The yield was still 90% even in the third runtime.

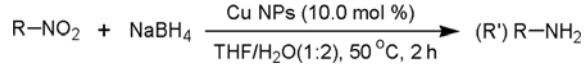
Table 2. Cu NPs catalyst's recyclable experiments

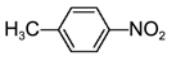
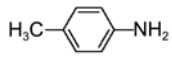
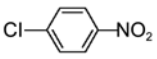
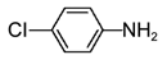
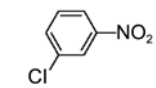
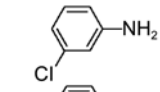
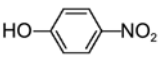
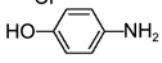
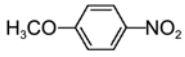
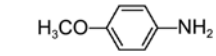
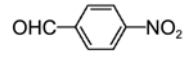
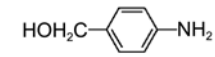
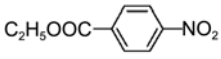
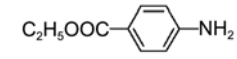
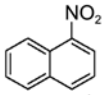
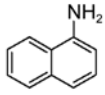
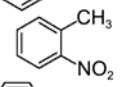
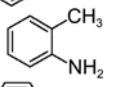
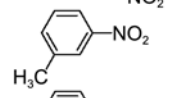
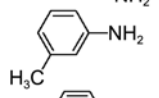
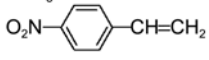
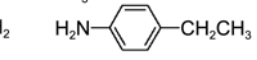
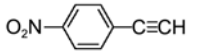
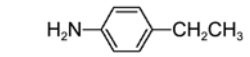
Runs	1	2	3
Isolated yield (%)	95	93	90

Furthermore, the recovery of the catalyst is easy to operate, which has a potential application on an industrial scale.

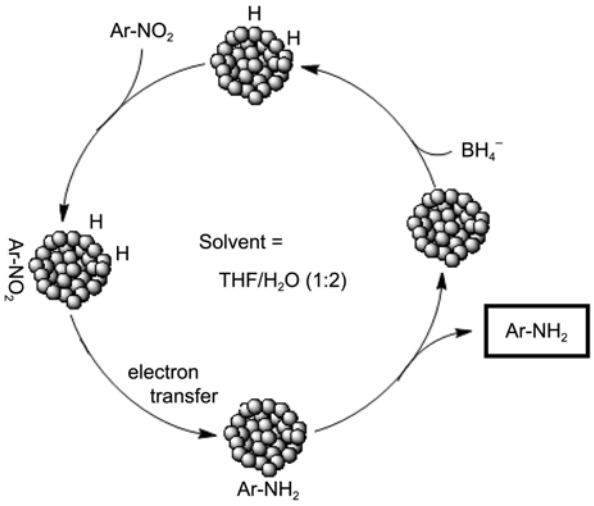
To expand the scope of the method, several representative aromatic nitro compounds were evaluated as substrates for nitro reduction reaction under the optimal condition. The results obtained are summarized in Table 3. Nitrobenzene with electron-donating substituents (Table 3, entries 1 and 5) or electron-withdrawing substituents (Table 3, entries 2 and 7) in para-position give the reduction products in high yields. Moreover, nitrobenzene with chlorine atom in *meta*-position (Table 3, entries 3), and nitrobenzene with methyl group atom in *ortho*- or *meta*-position (Table 3, entries 9 and 10) also display excellent conversion. From 4-nitrobenzaldehyde, 4-aminobenzyl alcohol can be obtained by simultaneous

Table 3. Reduction reactions of nitro aryl compounds[a]



Entry	Substrate	Product	Yield (%)[b]
1			91
2			95
3			95
4			66
5			90
6			92
7			86
8			89
9			87
10			91
11			82
12			90

[a]All the reactions were carried out with nitro aryl compounds (5.0 mmol) in the presence of copper NPs (10.0 mol %), $NaBH_4$ (3 equiv), and 10 mL THF/H_2O (1:2). [b]Yields of isolated products are the aveage of at least two experiments.



Scheme 1. Proposed mechanism for the reduction of aromatic nitro compounds.

reduction of nitro and aldehyde group (Table 3, entries 6). In addition, the reduction of 4-nitrophenol results in a moderate yield (66%) of 4-aminophenol (Table 3, entries 4). One reasonable explanation is separation difficult of the product due to the large polarity of hydroxyl groups. Importantly, this reduction strategy can be extended to 1-nitronaphthalene, which was converted to the corresponding product in good yield (Table 3, entries 8). Using 4-nitrostyrene or 1-ethynyl-4-nitrobenzene as substrate, it is found that not only nitro group but also C=C and C≡C can be reduced under the present conditions (Table 3, entries 11 and 12).

We speculated the proposed mechanism as showed in Scheme 1. It is in consistent with previous literatures.[21,22] In heterogeneous systems, it is demonstrated that there are four steps in the reduction of aromatic nitro compounds: (i) absorption of hydrogen, (ii) absorption of aromatic nitro compounds to the metal surfaces, (iii) electron transfer mediated by metal surfaces from BH_4^- to aromatic nitro compounds. (iv) desorption of aromatic amino compounds.

Conclusion

In summary, the Cu NPs we prepared not only has unique shape and structure, but also display an excellent catalytic property for the reduction of aromatic nitro compounds. Compared with the traditional methods of the nitro reduction, our procedure possesses lower cost, easier products separation, and higher yields. More importantly, the Cu NPs can be recycled and reused many times. On the basis of the above findings, further mechanistic investigation is currently in progress.

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