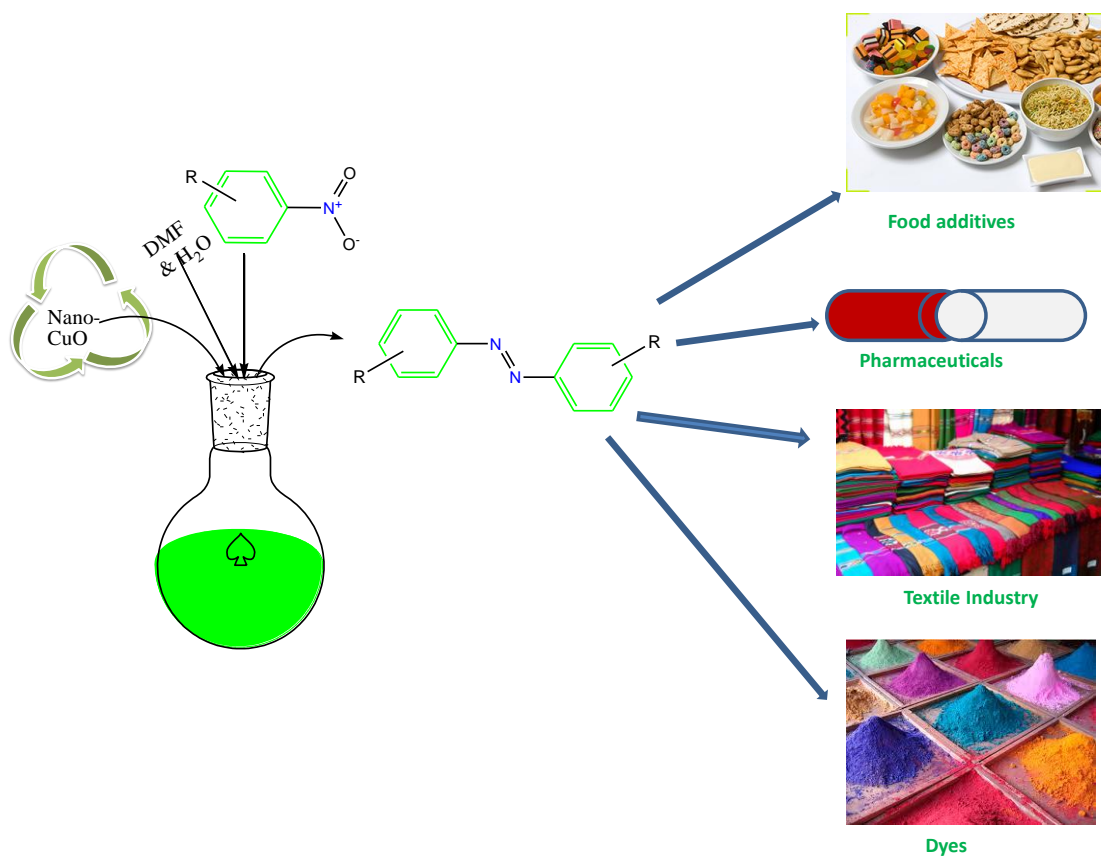


Chapter 5

A highly active copper(II) oxide nanoparticle catalyst for the synthesis of aromatic azo-compounds under mild conditions



Chapter 5

5.1 Introduction

Now-a-days aromatic azo-compounds are extensively used in industry as dyes, pigments, food additives and drugs.¹⁻³ Despite their importance, however, no current catalytic route offers high yields and selectivities. They are derived mainly through reduction of nitro-aromatics or by oxidation of anilines. The industrial production of aromatic azo-compounds (AroA) requires the coupling of diazonium salts with electron-rich aromatic compounds.⁴ Stoichiometric amounts of nitrite salts is required to form the diazonium salt and ironically, produces significant amounts of inorganic waste. Therefore, a sustainable, environment friendly and industrially applicable process for highly selective AroA is essential for fundamental and practical application. Previously, many researchers have attempted to make AroA by catalytic oxidation of amines.⁵ However, to utter disappointments, these approaches always require environmentally unfriendly transition metal catalysts. Examples include oxidation of aromatic amines with lead tetraacetate⁶ and reduction of nitroaromatics with lead metal.^{7,8} Therefore, AroA is synthesized today using stoichiometric reagents and environmentally unfriendly transition metals.⁹ A previous report on the catalytic oxidation of aniline with hydrogen peroxide using microporous crystalline titanosilicate (TS-1) showed that minimum amount of azobenzene formed instead of nitrosobenzene and azoxybenzene products.¹⁰ Recently, Merino¹¹ reviews various synthetic methods on AroA compounds. Jiao's group¹² demonstrated a novel approach for the synthesis of AroA compounds from the corresponding amines under mild conditions using CuBr and pyridine as a homogeneous catalyst.

Recently, some researchers have reported that NPs could be successfully used as catalyst to enhance the speed of a reaction in order to improve yield and less by-products.¹³ We have reported earlier that basic Al₂O₃ NPs catalyst could be used effectively for the *N*-formylation reaction under 'NOSE' approach.¹⁴ These applications seem to be motivated by the intention to enhance the catalytic efficiency through large surface areas of the NPs. However, a more intriguing aspect of the NPs catalysis arises from their size-specific electronic and geometric structures. Till now, to the best of our knowledge, there is no report of use of CuO NPs catalyst to synthesize AroA compounds by reduction of nitro aromatics.

Parts of this chapter have been communicated to an international journal

We demonstrate here a process with an environmentally benign NPs catalyst for the synthesis of AroA compounds by reduction of nito-aromatics under mild reaction conditions, with yields above 82%. Here, the catalyst CuO nanorod is synthesized through some modification from our earlier reported process¹⁵ in a very efficient, environment friendly wet chemical process and well characterized.

The solvent plays a major role in most of the organic reactions. Currently, in light of the environmental E factor,^{16,17} replacing toxic organic solvents with eco-friendly solvents like water is becoming a vital target of academic and scientific research. In our bodies, all physiological organic reactions take place in water and this spell-bounded fact has motivated chemists recently to develop clean and green protocols for organic transformations involving water as solvent. Inspiring by the fact, we have used a mixture of solvent involving water and *N,N*-dimethyl formamide (DMF) to synthesize AroA compounds under mild condition.

5.2 Experimental Section

5.2.1 Preparation of CuO NPs

Copper (II) oxide NPs have been synthesized following our earlier reported procedure with some modification to get uniform particles.¹⁵ Cupric Chloride (CuCl₂), Sodium Hydroxide (NaOH) and capping solvent were mixed in 2:1:2 ratio with 200 mL ethanol in a round bottom flask fitted with reflux condenser. The mixture was refluxed for 12 h and allowed to cool to room temperature. Then the mixture was again heated for 6 h. The product was washed with double distilled water and acetone repeatedly. The brown precipitate was centrifuged and washed with ethanol, acetone and hot water respectively. Finally, the product was dried at room temperature and heated to 120 °C and used for adsorption experiments.

5.2.2 General reaction procedure

A solution containing CuO NPs (10 mol%) and substituted nitrobenzene (1 mmol) in DMF:H₂O::2:1 (3 mL) was stirred at 100 °C for 12 h under aerobic condition. After the reaction was over (TLC), the reaction mixture was extracted with ethyl acetate and washed with double distilled water in a separating funnel. The organic layer was separated and collected in a conical flask. After evaporation of the solvent in a rotary evaporator, reaction mixture was subjected to column

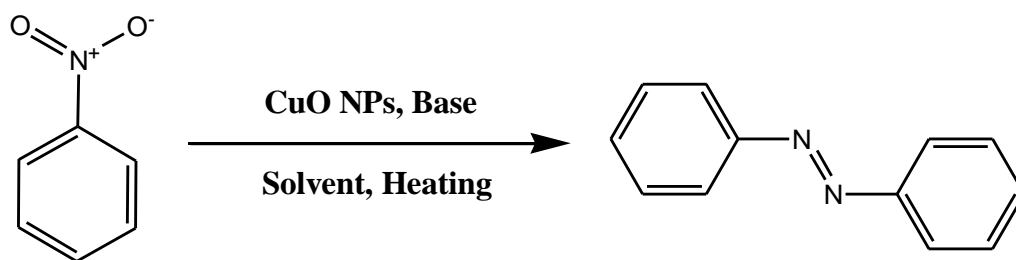
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chromatography on silica gel column (ethyl acetate/hexane, 1:10) to afford the respective product.

5.3 Results and discussion

5.3.1 Characterisation and optimization of reaction

In this paper, we report the heterogeneous CuO NPs catalysed synthesis of AroA compounds in air at 100 °C. In all the cases, it is found that CuO NPs is an efficient and environmentally-friendly heterogeneous, reusable catalyst. Optimization of reaction conditions was carried out taking same amount of the catalyst. Initially, nitrobenzene was selected as a model substrate with variation in solvent, time of reaction as well as base with the aim of optimizing the yield (Scheme 5.1) and the results are summarized in Table 5.1.



Scheme 5.1: Model reaction for the formation of azobenzene

All reactions were conducted at 100 °C under aerobic condition. Very less amount of products were found in the absence of a base (Table 5.1, entries 1-5). The reaction was performed with K₂CO₃ base varying different solvents and the yield of the azobenzene was found to increase in case of DMF-Water mixture (Table 5.1, entry 11). It is noteworthy that DMF and water mixture performs the role of solvent better when they are used in 2:1 ratio. Again, the reaction was subjected to variation in time in presence of K₂CO₃ and DMF:water::2:1 mixture solvent in order to get the optimized reaction time (Table 5.1). 85% of azobenzene was found in presence of K₂CO₃, and 15 mol%, CuO catalyst at 100 °C in DMF:water solvent within 12 h (Table 5.1, entry 11).

Table 5.1: Optimization of the reaction condition for solvent and time^a

Entry	Catalyst (15 mol%)	Solvent (3 mL)	Base (0.5 eqv.)	Time (h)	Yield ^b (%)
1	CuO NPs	MeOH	Nil	36	10
2	CuO NPs	<i>i</i> -PrOH	Nil	36	10
3	CuO NPs	H ₂ O	Nil	36	14
4	CuO NPs	DMF	Nil	36	10
5	CuO NPs	DMF:Water::2:1	Nil	36	20
6	CuO NPs	MeOH	K ₂ CO ₃	12	35
7	CuO NPs	<i>i</i> -PrOH	K ₂ CO ₃	12	15
8	CuO NPs	H ₂ O	K ₂ CO ₃	12	64
9	CuO NPs	DMF	K ₂ CO ₃	12	70
10	CuO NPs	Acetonitrile	K ₂ CO ₃	12	20
11	CuO NPs	DMF:Water::2:1	K₂CO₃	12	85
12	CuO NPs	DMF:Water::2:1	K ₂ CO ₃	1	10
13	CuO NPs	DMF:Water::2:1	K ₂ CO ₃	6	31
14	CuO NPs	DMF:Water::2:1	K ₂ CO ₃	24	86

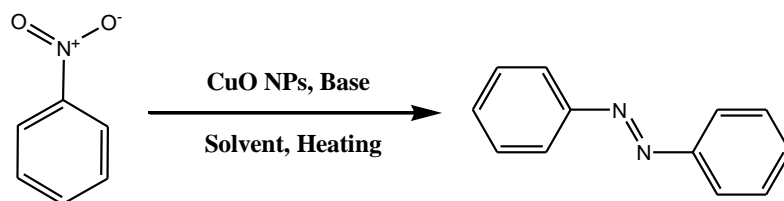
^aReaction condition: Nitrobenzene (1 mmol), temperature (100 °C), ^bIsolated yield of azobenzene

Keeping the solvent combination fixed, different bases were used and best result was obtained in case of K₂CO₃ (0.5 eqv.). It was found to have ~85% yield in presence of K₂CO₃ (0.5 eqv.) base and DMF:water (Table 5.2, entry 1).

The yield of azobenzene was also influenced by a variation of catalyst amount. It was noted that yield increased rapidly with an increase in the amount of the catalyst. We have taken CuO NPs catalyst in mol% and it was found that as the amount of catalyst was increased to 10 mol%, azobenzene formed in reasonably good yield and the further addition of catalyst had no significant effect over the yield of azobenzene (Table 5.3). That is, an increase in 5 mol% of catalyst increased the yield only by 3% (table 5.3, entry 1). So, from the economic point of view, 10 mol% catalyst was suitable one and we further proceeded with that amount.

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Table 5.2: Azobenzene formation from nitrobenzene varying different bases^a

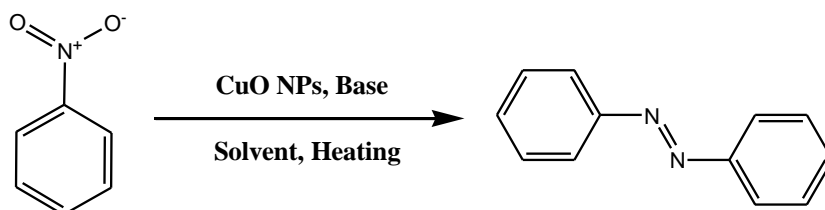


Entry	Catalyst (15 mol%)	Solvent (2:1, mL)	Base	Amount of base	Time (h)	Yield ^b (%)
1.	CuO	DMF:Water	K₂CO₃	0.5 eqv.	12	85
2.	CuO	DMF:Water	Na ₂ CO ₃	0.5 eqv.	12	65
3.	CuO	DMF:Water	Cs ₂ CO ₃	0.5 eqv.	12	86
4.	CuO	DMF:Water	(C ₂ H ₅) ₃ N	0.5 eqv.	12	25
5.	CuO	DMF:Water	(CH ₃) ₃ CONa	0.5 eqv.	12	50
6.	CuO	DMF:Water	K ₂ CO ₃	0.1 eqv.	12	28
7.	CuO	DMF:Water	K ₂ CO ₃	0.3 eqv.	12	64
8.	CuO	DMF:Water	K ₂ CO ₃	0.7 eqv.	12	84
9.	CuO	DMF:Water	K ₂ CO ₃	1.0 eqv.	12	84

^aReaction condition: Nitrobenzene (1 mmol), Temperature (100 °C), ^bIsolated yield of azobenzene

The yield of azobenzene was also influenced by a variation of catalyst amount. It was noted that yield increased rapidly with an increase in the amount of the catalyst. We have taken CuO NPs catalyst in mol% and it was found that as the amount of catalyst was increased to 10 mol%, azobenzene formed in reasonably good yield and the further addition of catalyst had no significant effect over the yield of azobenzene (Table 5.3). That is, an increase in 5 mol% of catalyst increased the yield only by 3% (table 5.3, entry 1). So, from the economic point of view, 10 mol% catalyst was suitable one and we further proceeded with that amount.

Table 5.3: Optimization of reaction condition varying catalyst amount^a



Entry	Catalyst	mol%	Solvent (2:1, 3 mL)	Base (0.5 eqv.)	Time (h)	Yield ^b (%)
1	CuO NPs	15	DMF:Water	K ₂ CO ₃	12	85
2	CuO NPs	12	DMF:Water	K ₂ CO ₃	12	82
3	CuO NPs	10	DMF:Water	K₂CO₃	12	82
4	CuO NPs	9	DMF:Water	K ₂ CO ₃	12	77
5	CuO NPs	8	DMF:Water	K ₂ CO ₃	12	68
6	CuO NPs	7	DMF:Water	K ₂ CO ₃	12	51
7	CuO NPs	5	DMF:Water	K ₂ CO ₃	12	38
8	CuO NPs	3	DMF:Water	K ₂ CO ₃	12	18

^aReaction condition: Nitrobenzene (1 mmol), Temperature (100 °C), ^bIsolated yield of azobenzene

Table 5.4: Optimization of reaction condition with varying reaction temperature^a

Entry	Catalyst	Time (h)	Temperature (°C)	Yield ^b (%)
1	CuO NPs	12	rt (25)	10
2	CuO NPs	12	45	22
3	CuO NPs	12	60	42
4	CuO NPs	12	75	57
5	CuO NPs	12	90	78
6	CuO NPs	12	100	82
7	CuO NPs	24	100	84
8	CuO NPs	36	100	84

^aReaction condition: Nitrobenzene (1 mmol), Catalyst (10 mol%), solvent (3 mL), base (0.5 eqv.) ^bIsolated yield of azobenzene

It is found from Table 5.4 that yield of azobenzene was highest when reaction was performed at 100 °C and the reaction mixture was heated for 36 h to optimize the time of reaction under that condition. However, the yield was almost constant after 12 h of reaction.

Thus, reduction of nitrobenzene to form azobenzene was performed taking CuO NPs as catalyst in DMF:water under air for 12 h at 100 °C. It is noteworthy to mention that CuO NPs have been synthesized in wet chemical process through some modification compared to our earlier report¹⁵ and well characterized with the help of TEM, SEM, EDAX and XRD. From TEM analysis it is clear that the particle is of nanosize (Figure 5.1). TEM image clearly reveals very small size of CuO NPs (10-20 nm). SEM and EDAX images of CuO NPs are shown in Figures 5.2 and 5.3

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respectively. It was observed that CuO NPs well synthesized and their sizes lie within 20 nm.

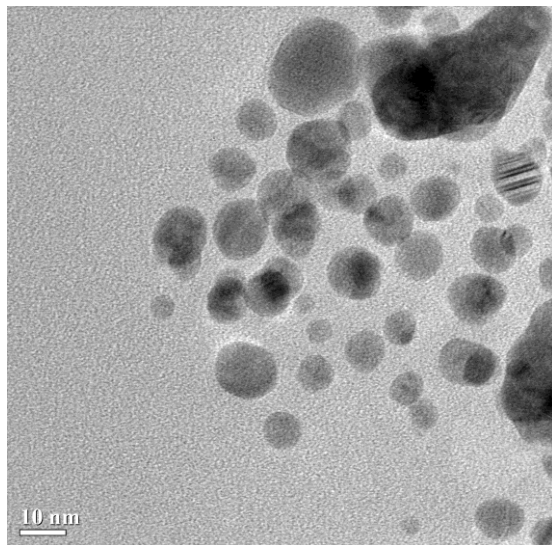


Figure 5.1: TEM image of CuO NPs

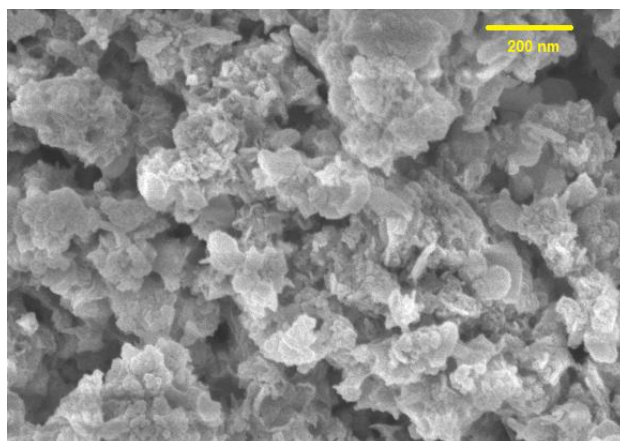


Figure 5.2: SEM image of CuO NPs

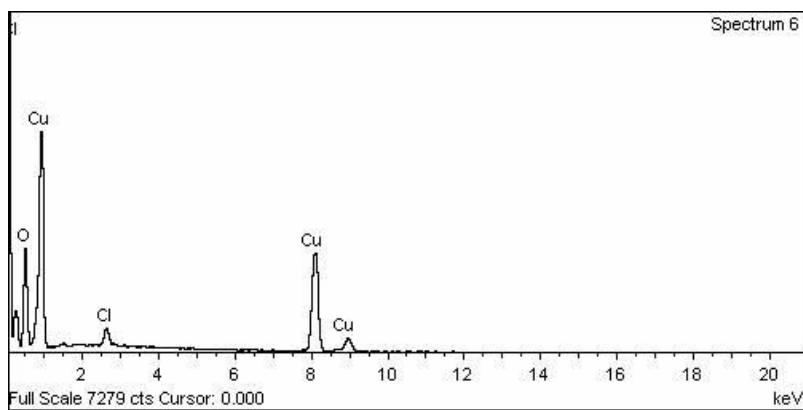
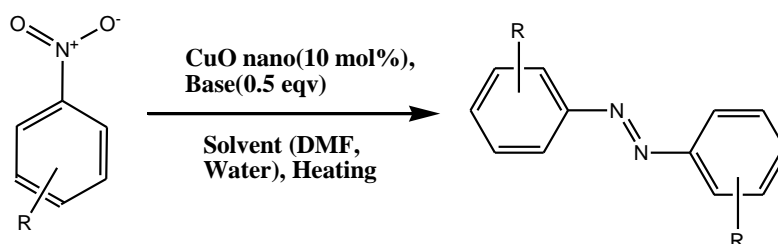


Figure 5.3: EDAX pattern of CuO NPs

Having defined the optimized reaction condition, we investigated the scope of the CuO NPs catalyzed azobenzene formation reaction with differently substituted nitrobenzene (Scheme 5.2) and the results are described in Table 5.5. As evident from Table 5.5, most of the substituted nitrobenzene afforded the products in good to excellent yields under the optimum reaction conditions (entries 1-10).

We investigated the formation of azobenzene from nitrobenzene bearing electron donating as well as electron withdrawing groups. Nitrobenzene bearing methyl, *tert*-butyl and methoxy groups gave desired products in 73–82% yields (Table 5.5, entries 2–7).



Scheme 5.2: General representative scheme for the synthesis of azobenzene

Table 5.5: Azobenzene formation from nitrobenzene with diversely substituted nitrobenzene^a

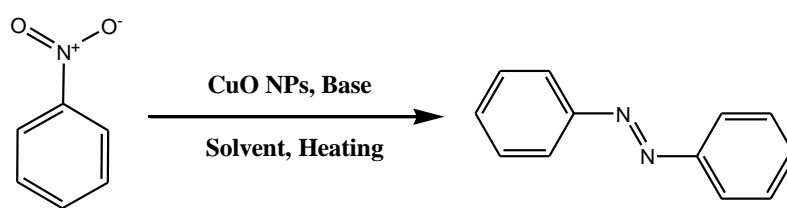
Entry	R	Products	Yield ^{b,c} (%)
1	H	Azobenzene	82
2	2-CH ₃	2,2'-Dimethylazobenzene	73
3	3-CH ₃	3,3'-Dimethylazobenzene	79
4	4-CH ₃	4,4'-Dimethylazobenzene	81
5	2-OCH ₃	2,2'-Dimethoxyazobenzene	75
6	4-OCH ₃	4,4'-Dimethoxyazobenzene	81
7	4- <i>tert</i> -butyl	4,4'-Di- <i>tert</i> -butylazobenzene	76
8	4-F	4,4'-Difluoroazobenzene	54
9	4-Cl	4,4'-Dichloroazobenzene	63
10	4-I	4,4'-Diiodoazobenzene	71

^aReaction condition: Nitrobenzene (1 mmol), CuO NPs (10 mol%), solvent (3 ml), K₂CO₃ (0.5 eqv.), ^bIsolated yield of azobenzene, ^cAll compounds were characterized by ¹H NMR and ¹³C NMR spectroscopy.

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Nitrobenzene bearing electron-withdrawing groups like fluoro, chloro and iodo groups provided corresponding azobenzene products in poor yields (54 –71 %; Table 5.5, entries 8–10). So, it is observed that electron donating groups enhance the yield of the products compared to electron donating groups. Careful inspection of the results revealed that *para*-substituted nitrobenzene with electron donating group yields better with respect to *ortho*-/*meta*-substituted reactant. As for example, the reaction of *p*-methyl nitrobenzene furnished the desired product 4,4'-dimethylazobenzene in 81% isolated yield (Table 5.5, entry 4), demonstrating good selectivity. *o*-methyl nitrobenzene produced the corresponding product 2,2'-dimethylazobenzene in lower yield of 73% (Table 5.5, entry 2). With a bulky group, 4-*tert*-butyl nitrobenzene, less amount of product was formed (Table 5.5, entry 7).

The transformation from nitrobenzene to azobenzene was carefully investigated over the time of the reaction based on GC analysis (Figure 5.4).



Scheme 5.3: Products profile of reduction of nitrobenzene

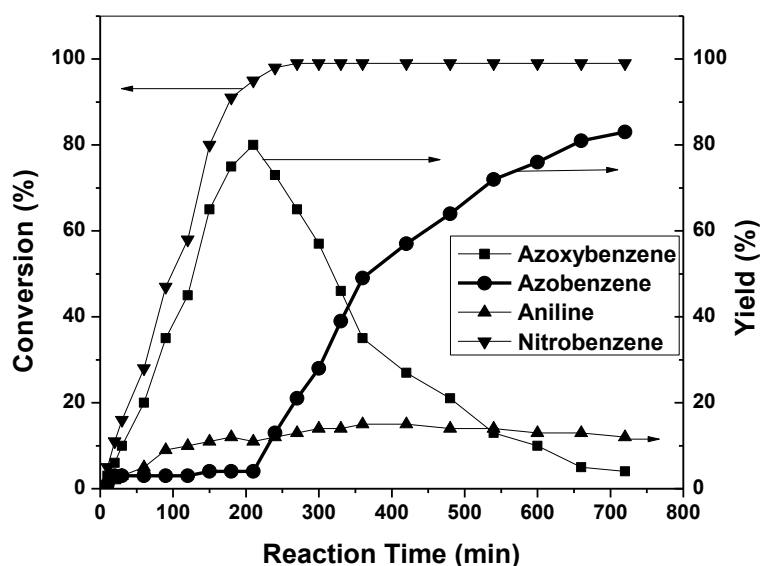
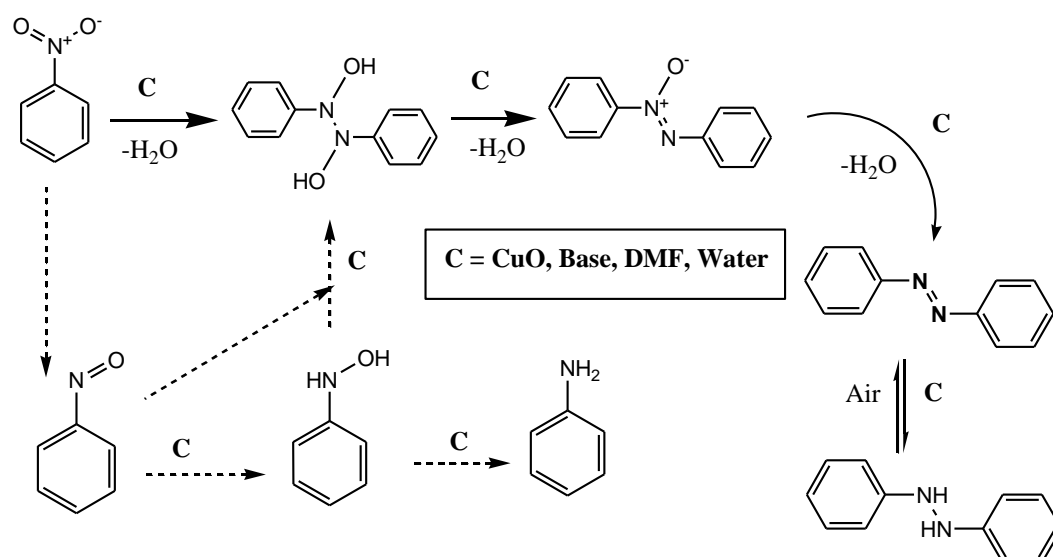


Figure 5.4: Time conversion plot for nitrobenzene reduction using CuO NPs

The amount of azoxybenzene was increased to a maximum at 3.5 h with the nitrobenzene being consumed in the reaction. With the progress of the reaction, more azoxybenzene was reduced to azobenzene, with the quantity of aniline almost remaining same. After 3.5 h of reaction time, azobenzene formation started and maximum yield was found after 12 h. Using this catalyst system, excellent yields of azobenzene can be achieved within 12 h.

We have proposed a probable mechanism for the azobenzene formation from nitrobenzene (Scheme 5.4) based on predicted mechanism reported by some other researchers.¹⁹ DMF acts as hydrogen source, the hydrogen is first adsorbed on the surface of CuO NPs and nitrobenzene is reduced to nitrosobenzene, which is instantly converted to *N*-hydroxybenzenamine.

Mechanism



Scheme 5.4: Plausible mechanism of the reaction

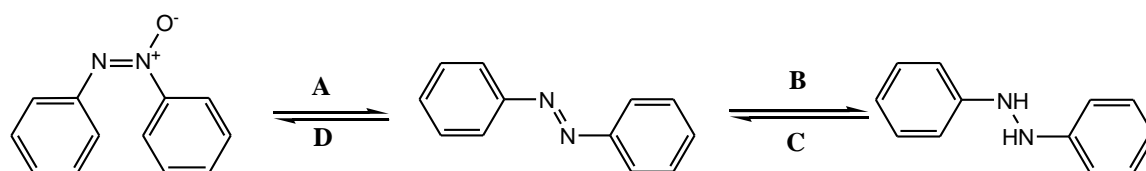
The *N*-hydroxybenzenamine can be further reduced to aniline under acidic or neutral conditions and cannot be revert back. However, in presence of K_2CO_3 in water (KOH is formed) i.e. mild basic condition, the *N*-hydroxybenzenamine primarily couples to nitrosobenzene to form *N,N'*-dihydroxy-diphenylhydrazine.²⁰ This dihydroxy intermediate is then readily dehydrated to produce azoxybenzene. But, in presence of air and hot reaction medium, azoxybenzene is not stable product. It is possible to interrupt the reaction at this moment, if azoxybenzene is the product of

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interest. Azoxybenzene can also be further reduced to azobenzene and then hydrazobenzene. But, hydrazobenzene spontaneously oxidizes to azobenzene in air. As a result, azobenzene is the only observed coupling product and the fact is supported by GC analysis.

Separately, it is found that hydrogenation of azoxybenzene can form azobenzene in high yield (Table 5.6, entry A1) which can be further reduced to form hydrazobenzene with extension of reaction time (Table 5.6, entry B1). Hydrazobenzene can be quantitatively converted back to azobenzene while heating in air at 100 °C for 6 h. Also, it is found that even in the absence of the nano catalyst, hydrazobenzene was converted to azobenzene with high yield (Table 5.6, entry C4). Overall, azobenzene is the major product from these transformations.

Table 5.6: Hydrogenation and oxidation of azobenzene^a



Entry	K ₂ CO ₃	Catalyst	Time (h)	Yield (%)
A1	Y	CuO NPs	6	98
B1	Y	CuO NPs	12	95
B2	N	CuO NPs	12	84
B3	Y	-----	12	Trace
C1	Y	CuO NPs	6	97
C2	Y	CuO NPs	12	97
C3	N	CuO NPs	6	93
C4	Y	-----	6	92
D	Y	CuO NPs	12	Trace

Y=Yes; N=No

^aReaction condition: Azobenzene (1 mmol), Catalyst (10 mol%), solvent (3 mL), Temperature: 100 °C, K₂CO₃ (0.5 eqv.)

5.3.2 Sheldon Test

The Sheldon test¹⁸ is a standard method to check whether a reaction is homogeneous or not. Therefore, we carried out Sheldon test to check whether the reaction was truly heterogeneous or due to some copper species present in the filtrate out of leaching. To perform Sheldon test, reaction time was chosen in such a way so that approx. half of the reaction was completed. The reaction was carried out under the optimized conditions varying time of the reaction and it was found that 46% product found after 6 h (Table 5.6).

Table 5.7: Sheldon test^a

Catalyst	Time (h)	Yield (%)	Time (h)	Yield ^b (%)
CuO NPs	1	12	-	-
CuO NPs	2	25	-	-
CuO NPs	4	34	-	-
CuO NPs	6	46	(6 + 6) = 12	46
CuO NPs	8	65	-	-
CuO NPs	10	72	-	-
CuO NPs	12	82	-	-

^aReaction condition: Nitrobenzene (1 mmol), Catalyst (10 mol%), solvent (3 mL), base (0.5 eq.) ^bIsolated yield of azobenzene

The CuO NPs catalyst was filtered off from the reaction mixture when 46% of azobenzene formed after 6 h. After removal of CuO catalyst, the filtrate was further stirred for an additional 6 h and no further azo-aromatic product was observed. Atomic absorption spectroscopy analysis of the filtrate from the reaction mixture and also of the filtrate from a stirred solution of CuO in water under identical reaction conditions confirmed no copper leaching. These results support the heterogeneous nature of the catalyst.

5.3.3 Reusability of catalyst

Reusability of the CuO NPs was investigated for better practical applicability (Figure 5.5). After completion of the reaction, the catalyst was recovered by filtration and washed with ethyl acetate & dry ethanol. The washed catalyst was heated at 120

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°C for 3 h and activated under vacuum at rt for 2 h, which was subsequently reused and the results are resented in Figure 5.5.

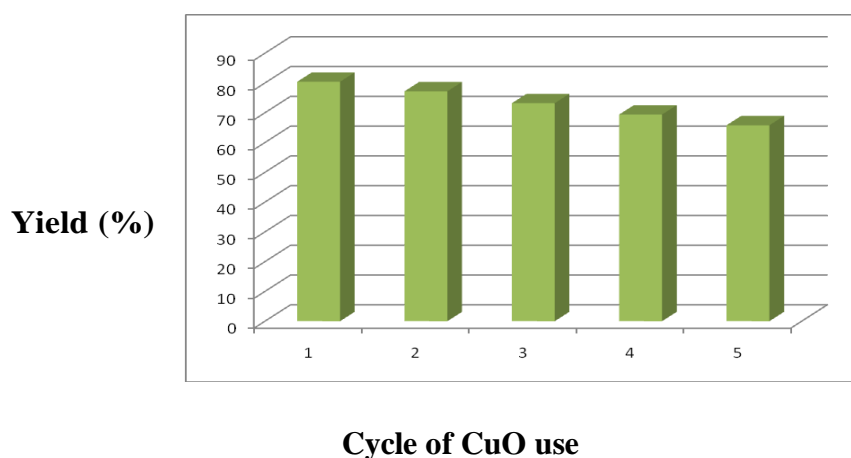


Figure 5.5: Reusability of CuO NPs catalyst

From this figure, it is clear that the decrease in the efficiency of the catalyst resulted in a minor loss of product yield even after five times of its reuse. Comparison of the powder XRD patterns of the fresh, reused CuO up to three and five times were also studied (Figure 5.6) which clearly showed that the reused catalyst exhibited a similar powder XRD pattern.

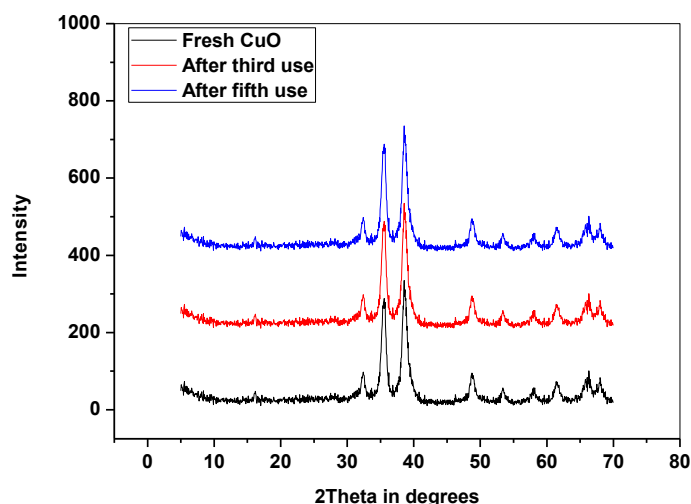


Figure 5.6: Powder XRD patterns of fresh and reused CuO NPs catalyst

The powder XRD pattern results clearly evidenced that no appreciable changes in the structural integrity during/after the reuse. To demonstrate the potential utility of this method for preparative purposes, the reaction was also carried out under the

optimized reaction conditions on a 12.30 g scale (0.1 mol of reactant), giving more than 81% yield which were comparable to those obtained for a small scale reaction (reaction condition: nitrobenzene, 200 mL DMF & water mixture, 100 °C, 12 h).

5.4 Conclusions

In conclusion, we have successfully developed a simple and efficient CuO NPs catalyzed methodology towards the formation of AroA compound directly from the corresponding nitroaromatic compounds. The reaction proceeds in economical and easily available solvent DMF and water under air in presence of a very mild base. The reaction is simple and efficient and does not require harmful transition metals, a fact which indirectly makes the AroA compounds preparation much facile and environmentally friendly. The synthesized CuO NPs remain in same condition even after performing the catalytic reaction. The catalyst is efficient, easily recoverable and reusable up to another four to five times without losing its activity appreciably. This protocol is relatively inexpensive and environmentally friendly manner. This reaction skips two-step synthesis of AroA compound from nitroaromatics and open a bright synthesis procedure.

References

1. Peter, A.P. & Freeman, H.S. *Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments*-Chap IV, Elsevier, London, 1991.
2. Catino, S.C. & Farris, E. *Concise Encyclopedia of Chemical Technology*, Wiley, New York, 1985.
3. Venkataraman, K. *The Chemistry of Synthetic Dyes*-Chap. VI, Academic Press, London, 1970.
4. (a) Frigerio, N.A., et al. *J. Chem. Educ.* **43**, 142, 1966. (b) Haghbeen, K. et al. *J. Org. Chem.* **63**, 4503--4505, 1998. (c) Gung, B.W., et al. *J. Chem. Educ.* **81**, 1630--1632, 2004. (d) Mosher, M.W., et al. *J. Chem. Educ.* **52**(3), 195, 1975.
5. (a) Baumgarten, H.E., et al. *J. Org. Chem.* **30**(4), 1203--1206, 1965. (b) Wenkert, K., et al. *J. Am. Chem. Soc.* **84**(24), 4914--4919, 1962. (c) Werkurt, E., et al. *Synth. Commun.* **18**(12), 1331--1337, 1988.
6. Firouzabadi, H., et al. *Bull. Chem. Soc. Jpn.* **56**, 914, 1983.
7. Ohe, K., et al. *J. Org. Chem.* **54**(17), 4169--4174, 1989.

Chapter 5

8. Osuka, A., et al. *Chem. Lett.* **12**, 1373, 1983.
9. Clark, J.H. *Chemistry of Waste Minimization*, Chapman & Hall, London, 1995.
10. Gontier, S., et al. *Appl. Catal. A: Gen* **118**, 173--186, 1994.
11. Merino, E. *Chem. Soc. Rev.* **40**, 3835--3853, 2011.
12. Zhang, C., et al. *Angew. Chem. Int. Ed.* **49**, 6174, 2010.
13. (a) Wang, L., et al. *Chem. Commun.* **48**, 5476, 2012. (b) Das, V.K., et al. *J. Org. Chem.* **78**(7), 3361--3366, 2013. (c) Das, V.K., et al. *Appl. Catal. A: Gen.* **456**, 118--125, 2012.
14. Das, V.K., et al. *Green Chem.* **14**(3), 847--854, 2012.
15. Raul, P.K., et al. *RSC Adv.* **4**(76), 40580--40587, 2014.
16. Lipshutz, B.H., et al. *Chem. Commun.* **50**(77), 11378--11381, 2014.
17. (a) Bechi, B., et al. *Green Chem.* **16**, 4524--4529, 2014. (b) Lipshutz, B. H., et al. *Green Chem.* **16**, 3660--3679, 2014.
18. Sheldon, R.A., et al. *Acc. Chem. Res.* **31**(8), 485--493, 1998.
19. Hu, L., et al. *Org. Lett.* **13**(20), 5640--5643, 2011.
20. Pizzolatti, M.G., et al. *J. Chem. Soc. Perkin Trans.*, **2**, 759--764, 1990. (b) Khan, F.A., et al. *Tetrahedron Lett.* **44**, 7783--7786, 2003. (c) Zhao, F., et al. *J. Catal.* **224**, 479--483, 2004. (d) Agrawal, A., et al. *Environ. Sci. Technol.* **30**, 153--160, 1996. (e) Shernyakin, M.M., et al. *Russ. Chem. Bull.* **6**, 1284--1293, 1957. (f) Russell, G.A., et al. *J. Am. Chem. Soc.* **89**, 3821--3825, 1967.
21. Food additives image in front page:
<https://www.google.co.in/search?hl=en-IN&q=food+additives&tbm=isch&tbs=simg:CAQSjAEaiQELEKjU2AQaAggFDAsQsIynCBpiCmAIAXIopRbJCaMWwwnICccJxAmkFqIWwg nMKagnyzSmIr4hyympJ6UgppmkIhowahHP4HXa6tXZdx90Akk2BY0sTH7L6v16CT3eCvMhYpE5D69ydJGPSD59eZJVAIsIAIMCxCOrv4I GgoKCAgBEgQTDHxQDA&sa=X&ved=0ahUKEwj19azHyqTJAhVG KZQKHQvsCfQQwg4IGSgA&biw=1366&bih=643>
22. Textile industry image in front page:
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dCtDA&ved=0ahUKEwiK8e7zyqTJAhUCi5QKHc49C6MQwg4IGSgA

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