Molecular Catalysis 492 (2020) 110998

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

One-pot synthesis of symmetrical and asymmetrical diphenylamines from guanidines with aryl iodide using Cu/Cu_2O nanocatalyst

Shivkumar R. Chaurasia, B.M. Bhanage*

Institute of Chemical Technology, Mumbai, 400019, India

ARTICLE INFO

Keywords:
Cu/Cu_2O
Biphenyl amine
Nano-catalysis
Guanidine
Recyclable

ABSTRACT

This work reports the selective one-pot synthesis of symmetrical and asymmetrical amines from guanidines as ammonia surrogate. The use of guanidine as ammonia source will eliminate the need of handling liquid ammonia. The reaction was performed using Cu/Cu_2O nanocatalyst under ligand-free condition. The synthesized catalyst was characterized by a various technique like XRD, FEG-SEM, HRTEM and XPS. The different diphenylamines are produced in good to very good yields. Recyclability study of catalyst shows that up to five cycles there is no significant loss in its activity.

Introduction

The utilization of copper based nanoparticles for organic synthesis has generated substantial interest in the field of catalysis due to their high catalytic activity, low cost and easy availability [1]. Although Cu and Cu_2O nanoparticles are showing a higher catalytic activity for various cross-coupling reaction than copper oxide (CuO) nanoparticles, they get easily oxidized by air or under the environment of reaction condition [2]. Several reports available prove that controlled synthesis of core-shell inorganic hybrid nanostructures such as Cu/Cu_2O leads to enhance catalytic activity compared to its component [3]. Su and co-worker have reported a $Cu@Cu_2O$ core–shell microspheres for dimethyldichlorosilane synthesis [4]. Recently, Yuan et al. has reported a Nb_2O_5 supported Cu/Cu_2O nanaoparticle for direct synthesis of alkynylphosphonates from alkynes and phosphite esters [5]. Meanwhile, Cu/Cu_2O has also been utilized as efficient visible light photo-catalysts due to efficient electron-hole pairs separation having application in photocatalysis dye degradation and hydrogen generation, etc. [6].

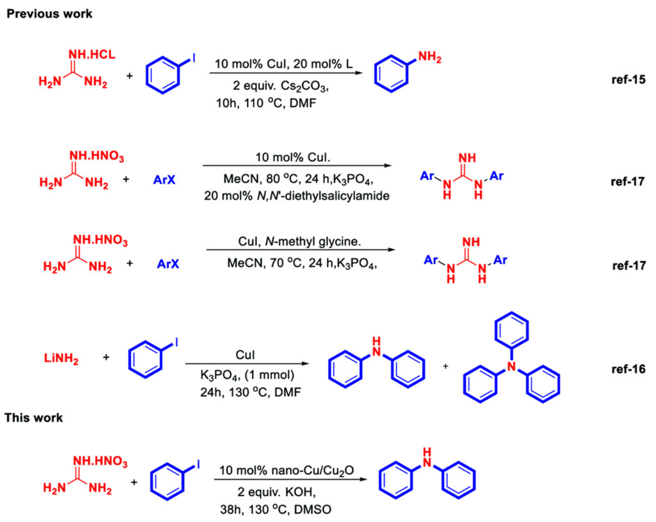
To date, various methods have been reported to synthesize Cu/Cu_2O core-shell nanostructures with well-defined morphologies such as cubes, octahedrons, tetrahexahedron, stars, and hollow structures [7]. Kamazani et al. has disclosed a solvent-free synthesis of $Cu–Cu_2O$ nanocomposites via green thermal decomposition route using novel precursor and investigation of its photocatalytic activity for degradation of MB under visible-light irradiation [8]. Ohiienko et. al has reported a polyol method for synthesis of uniform size Cu–CuO core–shell nanoparticle by double salt reduction [9]. Manideepa et al. has prepared a Cu/Cu_2O nanoparticle on nitrogen rich mesoporous carbon nanospheres and shows that interface is highly active for the hydroamination of aromatic terminal alkynes with aniline derivatives [10]. However, in most of these methods, either a template or capping agents are employed to control the growth and shape of nanoparticles. Also, sometimes it is difficult to completely remove the template or capping agent to get highly pure single-phase nanoparticles. On the other hand, the microwave assisted route for the synthesis of a nanoparticle is considered to be advantageous as it provides simple, fast and energy efficient way for the synthesis of a nanoparticle [11].

Diphenylamine and its derivatives constitute an extensive family of active compounds in pharmaceuticals, natural products, agrochemicals and materials science [12]. They have usually been prepared from the N-arylation of arylamines with aryl halides in the presence of transition metals such as Pd, Cu, Ni and Fe as a catalyst [13]. Efforts have been made to prepare diphenyl-amines selectively from ammonia with aryl halides [14]. However, the handling of ammonia is a tedious task and it causes high pressure inside the reaction vessel, obviously making the procedures not to be operationally safe and simple from the application's point of view. In 2008, Gao and co-workers have shown the use of amidine hydrochlorides as a new ammonia surrogate for the synthesis of a primary amine with various aryl halide in the presence of copper catalyst with suitable ligand [15]. In 2012, Tlili et al. have reported a method for the synthesis of both, symmetrical and asymmetrical arylated amines using $LiNH_2$ source of nitrogen [16]. Alternatively, copper-catalyzed *N,N'*-diarylation of guanidine has been documented by Antilla et al. and Ma et al. [17]. However, no reports are available for the synthesis of biaryl amine using guanidine as a nitrogen source. This method provides a one-pot selective synthesis of symmetrical or

---

* Corresponding author.
E-mail address: bm.bhanage@gmail.com (B.M. Bhanage).

https://doi.org/10.1016/j.mcat.2020.110998
Received 3 March 2020; Received in revised form 21 April 2020; Accepted 28 April 2020
2468-8231/



Scheme 1. Reaction of guanidine with aryl halides.

asymmetrical aryl amine using Cu/Cu_2O as a heterogeneous recyclable catalyst Scheme 1.

During the initial study, attempts were taken for the development of amidine based chemistry. Considering the principle of green and sustainable chemistry, we attempted this reaction in glycerol as a green solvent, 3 equiv. of inexpensive and easily available KOH base and prepared nano Cu/Cu_2O as a catalyst without using any additional ligand at 130 °C for 36 h. Surprisingly, no formation of *N,N*-diaryl guanidine could be noted, instead, there was a formation of aniline and diphenylamine. This inspired us to use guanidine nitrate as a new ammonia surrogate for the synthesis of symmetrical and asymmetrical diphenyl amines as there was no such report in the literature. Herein, we report simple one-pot synthesis of symmetrical diphenylamines and asymmetrical diphenylamines from guanidines in the presence of Cu/Cu_2O-nanocatalyst.

Experimental

Chemical

All the materials were obtained from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 and visualized using UV light. Column chromatography was performed with a silica gel (mesh 60–120).

Characterization

XRD pattern of synthesized materials was recorded using (Shimadzu XRD-6100 using CuKα-1.54 Å) with scanning rate 2θ per min and 2 theta (θ) angle ranging from 20 (θ) to 80 (θ) with current 30 mA and voltage 40 kW. The FT-IR spectra were recorded on Brucker Perkin Elmer-100 spectrometer in the wavelength range from 400 to 4000 cm^{-1}. Tescan MIRA 3 model with secondary electron (SE) detector was used for Field emission gun scanning electron microscopy analysis using 10.0 kV. The energy dispersive X-ray spectrum (EDS) was recorded by Oxford instrument (model 51-ADD0007). The GC–MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm) (column flow 2 mL min^{-1}, 100 °C–240 °C at 10 °C min^{-1} rise) was used for the mass analysis of the organic products. The yields of synthesize compounds were confirmed by Perkin Elmer Clarus 400 gas chromatography equipped with a flame ionization detector and a capillary column (elite-1, 30 m × 0.32 μm × 0.25 μm).

Preparation of Cu_2O catalyst

To a 100 mL aqueous solution of sodium thiosulfate ($Na_2S_2O_3$), 25 mL of copper sulphate ($CuSO_4{\cdot}5H_2O$) solution was added with continuous stirring. The molar ratio of copper sulphate to sodium thiosulfate and was maintained at 1:4. The resultant solution was then added to the 125 mL of 5 M NaOH solution with vigorous stirring. The obtained Cu_2O nanoparticles were then washed with deionized water and vacuum dried at 60 °C [18].

Preparation of Cu/Cu_2O nanocatalyst

Cu/Cu_2O nanoparticles were prepared by the method reported by Bhosale et al. [11]. To a glass beaker containing 10 mL of 1,3-propanediol, 0.4 g of $Cu(CH_3COO)_2{\cdot}H_2O$ was added. The resultant mixture was then kept inside a domestic microwave oven at an electric power of 600 W for 4 min with the on/off mode having a time interval of 30 s, color of reaction mixture changes from blue to brick-red indicating formation of Cu/Cu_2O nanoparticles.

Preparation of Cu° catalyst

0.4 g of $CuSO_4{\cdot}5H_2O$ was taken in a glass beaker containing 10 mL of 1,3-propanediol and 0.4 g of glucose. Then, other steps are same as that of Cu/CuO preparation [19].

Preparation of Cu/Cu_2O@Fe_3O_4 nanocatalyst

For the preparation of Cu/Cu_2O@Fe_3O_4 catalyst, 1.0 g of Fe_3O_4 was first dispersed in 10 mL of 1,3-propanediol using sonication for 30 min. To the resultant mixture 0.4 g of $Cu(CH_3COO)_2{\cdot}H_2O$ was added. Then, other steps are same as that of Cu/Cu_2O preparation.

General procedure for the nano Cu/Cu_2O catalyzed synthesis of diphenylamine

To a mixture of iodobenzene (1.0 mmol), guanidine nitrate (0.5 mmol), and KOH (3.0 mmol) in DMSO (2 mL), Cu/Cu_2O (25 mg) was added. The resulting mixture was then sealed and stirred for 36 h at 130 °C. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with water followed by extraction using ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporation of the solvent on rotavapor. The residue was purified by column chromatography with ethyl acetate and pet-ether as eluent to give the pure product.

Results and discussion

Crystallinity and phase information of the synthesize Cu/Cu_2O NP was examined by the X-ray diffraction (XRD) pattern. Fig. 1 depicts the XRD pattern of the prepared Cu/Cu_2O nanocatalyst. The peaks at 2θ values of 43.30°, 50.43°, 74.13° correspond to the reflections of (111), (200) and (220) planes of cubic Cu^o with lattice constant of a = 3.615 Å (d-spacing = 0.2090 nm) and diffraction peaks at 2θ values 29.5°, 36.4°, 42.3°, 61.3°, 73.5°, 77.3° can be ascribed to the (110), (111), (200), (220), (311), (222) planes of cubic Cu_2O (d-spacing = 0.2469 nm), respectively. The sharp peaks in the pattern indicate that the Cu/Cu_2O NPs are highly crystallized. The absence of peak for CuO indicates that the prepared catalyst is Cu/Cu_2O. SEM images of synthesized nanoparticles were taken to examine the surface morphology. From Fig. 2 we can see that Cu/Cu_2O NP is having an irregular shape morphology and particle in size ranges of 60 – 120 nm. The chemical composition of the synthesized Cu/Cu_2O NPs was examined by energy dispersive spectroscopy (EDS). Spectra at different position were recorded to find the average composition of the Cu/Cu_2O NPs. The presence of only oxygen and copper peak indicates the prepared

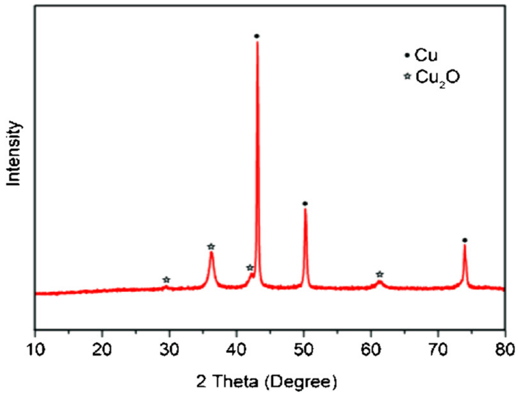


Fig. 1. XRD pattern of Cu/Cu_2O NPs.

nanomaterial is pure and free from other metal impurities (see ESI Fig. 2(b)).

To distinguish two different Cu phases HRTEM image was taken. From Fig. 3, we can see that two different lattice fringes are having an interlayer spacing of 0.21 nm and 0.25 nm which can be ascribed to the (311) lattice plane of Cu^0 and (111) lattice plane of Cu_2O respectively.

XPS was carried out to study the surface chemical nature of synthesized Cu/Cu_2O nanoparticles. Fig. 4a shows the typical XPS spectra of Cu/Cu_2O NP ranging from 0 to 1400 eV. The presence of respective peak for Cu, C and O in the survey spectrum confirms that the prepared sample contains Cu, C and O only. The copper 2p peaks at binding energies of 953.1 and 932.6 eV can be attributed to the binding energy of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ respectively. The satellite peak at 942.9 eV and 963.7 eV was also observed. However, due to very small differences in the binding energy of Cu^{1+} (Cu_2O) and Cu^0 by XPS it is difficult to differentiate between them (Fig. 4b).

The core-level O1 s spectrum is shown in Fig. 4(c). Oxygen 1 s peak observed at 530.1 eV represent lattice oxygen in Cu_2O. Thermal stability of Cu/Cu_2O nanocatalyst was determined by DSC-TGA analysis. A weight loss was observed near 100 °C which can be due to presence of moisture absorbed on the surface. A weight gain was observed near 250 °C which can be due to oxidation of metallic copper to copper oxide (see ESI Fig. 2(a)).

After thoroughly characterizing the catalyst it was tested for its catalytic activity. From Scheme 2 we can see that three different product are possible on reaction of iodobenzene with guanidine nitrate.

Initially, iodobenzene (**1a**, 2.0 mmol) with guanidine nitrate (**2a**, 0.75 mmol) were chosen as model substrates. The reaction conditions were optimized using various reaction parameters and include catalyst, base, solvent, temperature and time. Only 35% of diphenylamine (**3aa)** was formed when the reaction was performed using Cu_2O catalyst in glycerol at 130 °C for 36 h (Table 1, entry 1). Interestingly, addition of DMSO led to a noticeable increase in the yield of **3aa** to 44% (Table 1, entry 2). A further increase in the yield of product **3aa** was noted when reaction was performed in only DMSO however, addition of ligand L-proline led to a slight decrease in the yield this could because of change in the solvent media system (Table 1, entry 3). Other Cu-catalyst such as CuI, CuBr and CuO were also screened but they were not found to be active to increase in the yield of **3aa** (Table 1, entries 4–6). Next, an attempt was made to carry out this reaction using nano-Cu/Cu_2O (Table 1, entry 7), a significant increase in the yield was noted producing highest 88% yield of **3aa**. Further, to check whether only Cu° or Cu_2O is sufficient to catalyze the reaction. Both Cu° and Cu_2O nanocatalyst were prepared and employed for this reaction individually (Table 1, entries 8, 9). As per our expectation both the catalysts furnished the desired product however a relatively lower yield of 3aa was

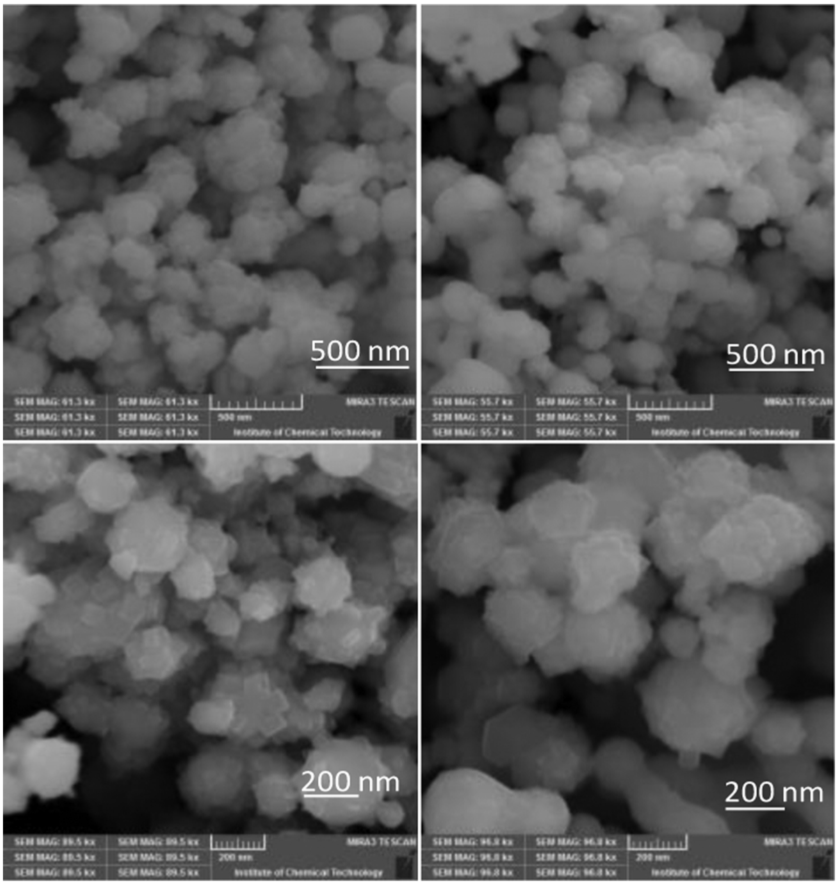


Fig. 2. SEM images of Cu/Cu_2O NPs.

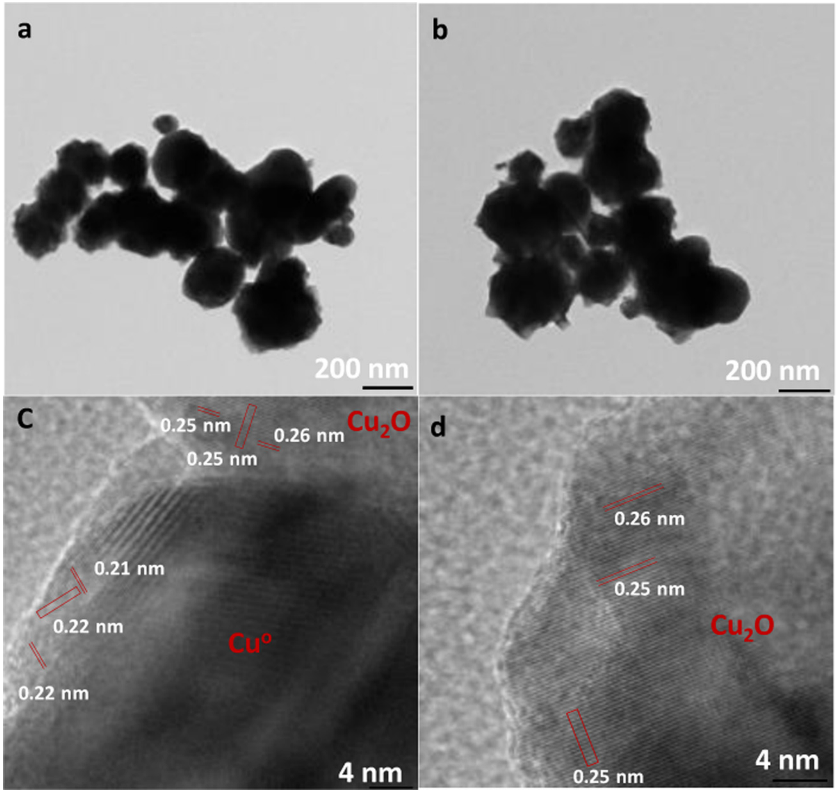


Fig. 3. (a, b) TEM images of Cu/Cu_2O NPs, (c) HR-TEM image of Cu/Cu_2O with lattice spacing, (d) HR-TEM image of Cu_2O nanoparticle with lattice spacing.

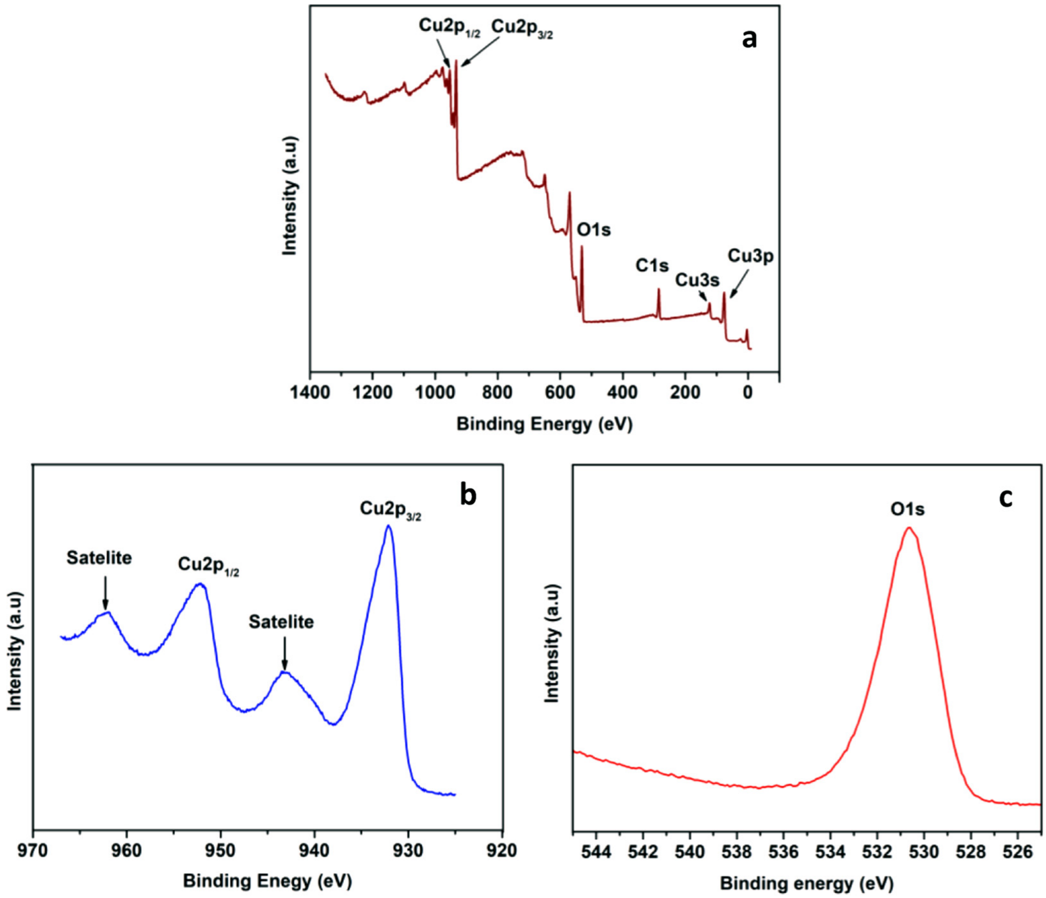
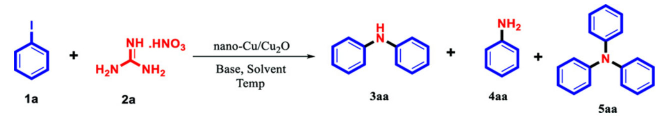


Fig. 4. XPS mapping of Cu/Cu_2O NPs (a) survey spectra of Cu/Cu_2O; (b) high-resolution spectra of $Cu_2p_{3/2}$; (c) high-resolution spectra of O1 s.



Scheme 2. Synthesis of diphenylamine with other possible side product.

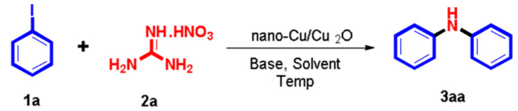
observed with nano-Cu_2O catalyst. To further improve the catalyst separability Cu/Cu_2O nanoparticles loaded on Fe_3O_4 were prepared and used as a catalyst, however lower yield was obtained (Table 1, entry 10). While studying the effect of catalyst loading on yield it was observed that decrease in the catalyst loading to 15 mol% led to decrease in the yield of product **3aa** and on the other hand increase in the catalyst loading did not have any considerable effect on the reaction. (Table 1, entry 1112) Three mmol of KOH was found to be crucial for this reaction providing 88% yield of 3aa on other hand performing the reaction with two mmol and one mmol of KOH resulted into formation of only 74 and 44% yield of 3aa respectively. (Table 1, entry 13, 14) Other inorganic bases such as K_2CO_3 and Na_2CO_3 were also screened providing **3aa** in poor yields (Table 1, entries 15, 16). The reaction also resulted in the formation of a 66% yield in solvent DMF (Table 1, entry 17). While studying the effect of time on product yield it was observed that cessation of reaction for the shorter duration gives aniline as a major product. However, prolonging the reaction duration does not have any effect on the yield of diphenylamine (Table 1, entry 18–21) Changing reaction environment from N_2 to air leads to a lower yield of the product (Table 1, entry 22)

The optimized reaction conditions are, 10 mol% Cu/Cu_2O, (confirm) 20 mol, 3 equiv. of KOH, 1 mmol of guanidine nitrate (**1a**) and 2 mmol of iodobenzene (2), DMSO as the solvent at 130 °C under a nitrogen atmosphere for 36 h. To demonstrate the advantages of developed catalytical system different derivatives of iodobenzene were allowed to react with guanidine nitrate to gives symmetrical amine. The electron-donating group methyl, methoxy were furnishing the desired product in good yield however with electron-withdrawing group like nitro (NO_2) only 4-nitroaniline was observed as a major product and along with the trace of coupling product. A derivative of guanidine was also tested to get asymmetrical diphenylamine (Table 2).

While using the substituted guanidine it was expected to get a mixture of symmetrical and asymmetrical diphenylamine due to liberation of ammonia by hydrolysis along with arylamine as shown in Scheme 3. However, only corresponding diphenylamine was observed as a major product. Different asymmetrical diphenylamines were synthesized in good to excellent yields. using diphenyl guanidine as a coupling partner along with substituted iodobenzene (Table 2). Similarly substituted urea was also used for the synthesis of asymmetrical amine. A good yield of product was observed which also indicate that decomposition of guanidine nitrate results in the formation of urea which on further decomposition gives another molecule of corresponding ammonia or arylamine. Although a detailed mechanism for this transformation is still unclear, we proposed a possible catalytic cycle as outlined in Fig. 5 Fig. 6. Initially, iodobenzene and Cu/Cu_2O give intermediate-I via oxidative addition. At higher temperature, the presence of base leads to the thermal decomposition of guanidine to give ammonia and one molecule of urea as reported by Limatibul et al., Homer et al. and Lewis et al. [20] The ammonia liberated is then in presence of intermediate I to gives respective aniline liberating 1 molecule of hydrogen halide. Aniline formed is then attacked by another molecule of iodobenzene and catalyst via oxidative addition to give intermediate-II with the release of another molecule of hydrogen halide. The product diphenylamine is then liberated from the catalytic system by reductive elimination and catalyst is regenerated [21]. However, in the case of substituted guanidine, its decomposition gives corresponding amine with urea as a decomposition product which then reacts with one molecule of iodobenzene to give diphenylamine. The formation of aniline was also confirmed by GC—MS by carrying out the reaction for the shorter duration.

To validate the heterogeneous nature of the Cu/Cu_2O catalyst hot filtration experiment was carried out. In the first set of experiment, catalyst was filtered off ; after 12 h at 130 °C, allowing the remaining

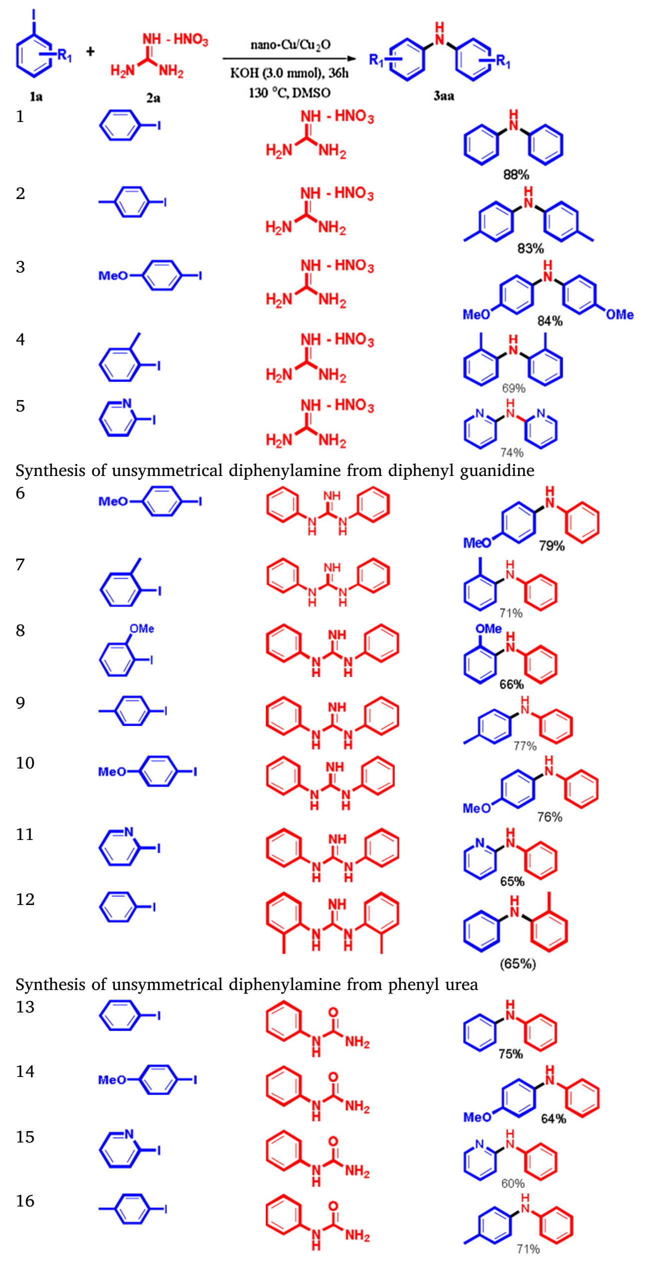
Table 1
Optimization of reaction parameter for the synthesis of diphenylamine[a.]



Entry	Catalyst (mol%)	Base (mmol)	Time (hr)	Solvent	Yield[b] (%)
1	Cu_2O (20)	KOH (3)	36	Glycerol	35
2	Cu_2O (20)	KOH (3)	36	Glycerol : DMSO	44
3[c]	Cu_2O (20)	KOH (3)	36	DMSO	55
4	CuI (20)	KOH (3)	36	DMSO	38
5	CuBr (20)	KOH (3)	36	DMSO	32
6	CuO bulk	KOH (3)	36	DMSO	43
7	Nano-Cu/Cu_2O (20)	KOH (3)	36	DMSO	88
8	Nano-Cu^o (20)	KOH (3)	36	DMSO	65
9	Nano-Cu_2O (20)	KOH (3)	36	DMSO	50
10	Nano-Cu/Cu_2O @Fe_3O_4	KOH (3)	36	DMSO	67
11	Nano-Cu/Cu_2O (15)	KOH (3)	36	DMSO	76
12	Nano-Cu/Cu_2O (30)	KOH (3)	36	DMSO	89
13	Nano-Cu/Cu_2O	KOH (2)	36	DMSO	74
14	Nano-Cu/Cu_2O (20)	KOH (1)	36	DMSO	44
15	Nano-Cu/Cu_2O (20)	K_2CO_3 (2)	36	DMSO	42
16	Nano-Cu/Cu_2O	Na_2CO_3 (2)	36	DMSO	39
17	Nano-Cu/Cu_2O	KOH (3)	36	DMF	66
18	Nano-Cu/Cu_2O	KOH (3)	12	DMSO	20
19	Nano-Cu/Cu_2O	KOH (3)	24	DMSO	50
20	Nano-Cu/Cu_2O	KOH (3)	30	DMSO	80
21	Nano-Cu/Cu_2O	KOH (3)	40	DMSO	87
22[d]	Nano-Cu/Cu_2O	KOH (3)	36	DMSO	75

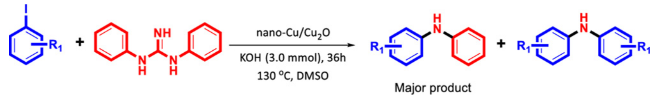
[a] Reaction condition: (**1a**) (2 mmol), (**2a**) (0.75 mmol), catalyst (10 mol %), solvent (2 mL) temp 130 °C, time 36 h. under N_2 atmosphere. [b] GC yield based on area. [c]Use of proline as ligand. [d] Reaction carried out under air atmosphere.

Table 2
Substrate study of diphenylamine derivative.



Entry	Yield
1	88%
2	83%
3	84%
4	69%
5	74%
Synthesis of unsymmetrical diphenylamine from diphenyl guanidine	
6	79%
7	71%
8	66%
9	77%
10	76%
11	65%
12	(65%)
Synthesis of unsymmetrical diphenylamine from phenyl urea	
13	75%
14	64%
15	60%
16	71%

Reaction condition: (**1a**) (2 mmol), (**2a**) (1 mmol), Cu/Cu$_2$O catalyst (20 mg), base (3 equiv.), DMSO (2 mL), 130 °C for 36 h.



Scheme 3. Synthesis of asymmetrical diphenylamine and related product.

solution to react further under identical conditions whereas in another vessel reaction was continued without taking out catalyst. No progress was observed in the first reaction vessel however complete yield was obtained in the second reaction vessel.

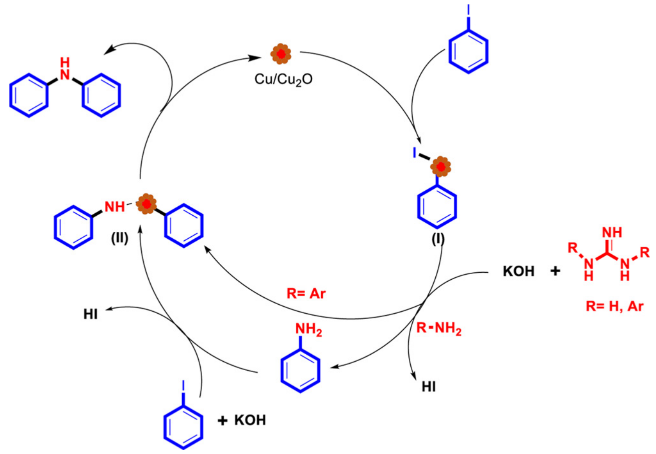


Fig. 5. Plausible reaction mechanism for biarylamine synthesis.

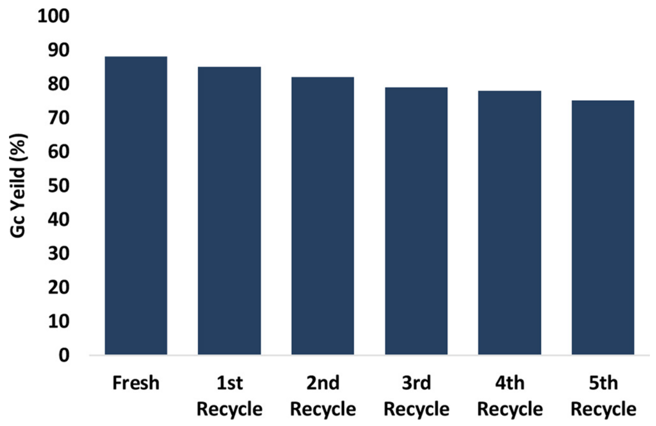


Fig. 6. Recyclability study of Cu/Cu$_2$O. (a) Reaction conditions: (**1a**) (2 mmol), (**2a**) (1 mmol), Cu/Cu$_2$O catalyst (30 mg), base (3 equiv.), DMSO (2 mL) at 130 °C for 36 h.

Catalyst recycling

To established the recyclability of catalytic system. After completion of reaction, catalyst was separated from reaction mixture by filtration and washed with water-ethanol mixture several times followed by drying at 80 °C. The resultant catalyst is and then used for further reaction. To compensate the handling loss while recovering the catalyst from reaction mixture fresh catalyst was added to during each cycle. From the graph, we can see that there is no significant drop in the significant drop in the catalyst activity up to five cycles.

Conclusions

In summary, a simple method showing the use of guanidine as an ammonia surrogate was reported for one-pot synthesis of various symmetrical or asymmetrical di- using aryl halides. The reaction was performed using Cu/Cu$_2$O nanocatalyst under ligand-free condition and eliminates the need for expensive catalysts and ligands. The synthesized catalyst was characterized by various techniques like XRD, FEG- SEM, HRTEM, XPS. The different diphenylamines are produced in good to very good yields. The catalyst was recycled up to 5 cycles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Shivkumar R. Chaurasia: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing - original draft. **B.M. Bhanage:** Conceptualization, Methodology, Writing - review & editing, Supervision, Validation, Resources, Funding acquisition.

Acknowledgements

The author Shivkumar R. Chaurasia is greatly thankful to the University Grant Commission (UGC), New Delhi, India for providing a UGC-BSR fellowship and Abhishek Tiwari for his help in preparing the manuscript.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110998.

References

[1] (a) M.B. Gawande, A. Goswami, F.X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R.S. Varma, Chem. Rev. 116 (2016) 3722–3811;
(b) A.B. Raut, B.M. Bhanage, Chem. Select 2 (2017) 10055–10060;
(c) A.B. Raut, A.R. Tiwari, B.M. Bhanage, ChemCatChem 9 (2017) 1292.

[2] T. Yuan, Fei Chenb, Lu Guo-ping, New J. Chem. 42 (2018) 13957–13962.

[3] (a) I. Kim, Y. Kim, K. Woo, E.-H. Ryu, K.-Y. Yon, G. Cao, J. Moon, RSC Adv. 3 (2013) 15169–15177;
(b) D. Chen, C. Li, H. Liu, et al., Core-shell Au@Pd nanoparticles with enhanced catalytic activity for oxygen reduction reaction via core-shell Au@Ag/Pd constructions, Sci. Rep. 5 (2015) 11949;
(c) R.G. Chaudhuri, S. Paria, Core/Shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications, Chem. Rev. 112 (4) (2012) 2373–2433.

[4] Tao Yuan, Fei Chen, Guo-ping Lu, New J. Chem. 42 (2018) 13957–13962.

[5] Z. Zhang, H. Che, Y. Wang, J. Gao, Y. Ping, Z. Zhong, F. Su, Chem. Eng. J. 211 (2012) 421–431.

[6] (a) W. Chen, Z. Fan, Z. Lai, J. Mater. Chem. A Mater. Energy Sustain. 1 (2013) 13862–13868;
(b) H. Devnani, N. Rashid, P.P. Ingole, ChemistrySelect 4 (2019) 633–643;
(c) M. Yurderi, A. Bulut, I.E. Ertas, M. Zahmakiran, M. Kaya, Appl. Catal. B Environ. 165 (2015) 169–175;
(d) M. Li, X. Xing, Z. Ma, J. Lv, P. Fu, Z. Li, ACS Sustain. Chem. Eng. 6 (2018) 5495–5503;
(e) S.B. Kalidindi, U. Sanyala, B.R. Jagirdar, Phys. Chem. Chem. Phys. 10 (2008) 5870–5874.

[7] A. Radi, D. Pradhan, Y. Sohn, K.T. Leung, ACS Nano 4 (2010) 1553–1560.

[8] M. Mousavi-Kamazani, Z. Zarghami, R. Rahmatolahzadeh, M. Ramezani, Adv. Powder Technol. 28 (2017) 2078.

[9] O. Ohiienko, Y.J. Oh, Mater. Chem. Phys. 218 (2018) 296–303.

[10] M. Sengupta, S. Das, A. Bordoloi, Mol. Catal. 440 (2017) 57–65.

[11] (a) B.A. Dreikorn, K.E. Kramer, D.F. Berard, R.W. Harper, E. Tao, L.G. Thompson and J.A. Mollet, 1992, 336–341.
(b) M.B. Gawande, S.N. Shelke, R. Zboril, R.S. Varma, Acc. Chem. Res. 47 (2014) 1338–1348;
(c) M.A. Bhosale, T. Sasaki, B.M. Bhanage, Catal. Sci. Technol. 4 (2014) 4274–4280;
(d) M.A. Bhosale, S.C. Karekar, B.M. Bhanage, Chem. Select 1 (2016) 6297;
(e) M.A. Bhosale, B.M. Bhanage, RSC Adv. 4 (2014) 15122–15130

[12] (a) P. Paul, R.J. Butcher, S. Bhattacharya, Inorg. Chim. Acta 425 (2015) 67–75;
(b) I. Güell, X. Ribas, Eur. J. Org. Chem. 15 (2014) 3188–3195;
(c) C. Singh, J. Rathod, V. Jha, A. Panossian, P. Kumar, F.R. Leroux, Eur. J. Org. Chem. 2 (2015) 6515–6525;
(d) M.S. Siddegowda, H.S. Yathirajan, R.A. Ramakrishna, Tetrahedron Lett. 53 (2012) 5219–5222;
(e) A.K. Gupta, G.T. Rao, K.N. Singh, Tetrahedron Lett. 53 (2012) 2218;
(f) P.K. Khatri, S.L. Jain, Tetrahedron Lett. 54 (2013) 2740–2743;
(g) H. Veisi, S. Hemmati, H. Javaheri, Tetrahedron Lett. 58 (2017) 3155.

[13] (a) Q. Shen, John F. Hartwig, J. Am. Chem. Soc. 128 (31) (2006) 10028–10029;
(b) D.S. Surry, S.L. Buchwald, J. Am. Chem. Soc. 129 (2007) 10354;
(c) Q. Shen, J.F. Hartwig, J. Am. Chem. Soc. 128 (2006) 10028;
(d) F. Lang, D. Zewge, I.N. Houpis, R.P. Volante, Tetrahedron Lett. 42 (2001) 3251;
(e) N. Xia, M. Taillefer, Angew. Chem., Int. Ed. 48 (2009) 337.

[14] Y. Aubin, C. Fischmeister, C.M. Thomas, J.-L. Renaud, Chem. Soc. Rev. 39 (2010) 4130–4145.

[15] X. Gao, H. Fu, R. Qiao, Y. Jiang, Y. Zhao, J. Org. Chem. 73 (17) (2008) 6864–6866.

[16] A. Tlili, F. Monnier, M. Taillefer, Chem. Commun. 48 (2012) 6408–6410.

[17] (a) M. Cortes-salva, B. Nguyen, J. Cuevas, K.R. Pennypacker, J.C. Antilla, Org. Lett. 12 (6) (2010) 1316–1319;
(b) H. Xing, Y. Zhang, Y. Lai, Y. Jiang, D. Ma, J. Org. Chem. 77 (12) (2012) 5449–5453.

[18] L. Xiong, H. Yu, C. Nie, Y. Xiao, Q. Zeng, G. Wang, B. Wang, H. Lv, Q. Lia, S. Chen, RSC Adv. 7 (2017) 51822.

[19] (a) U.S. Shenoy, A.N. Shetty, Appl. Nanosci. 4 (2014) 47–54;
(b) V. Andal, G. Buvaneswari, Eng. Sci. Technol. Int. J. 20 (2017) 340–344;
(c) L.S.B. Upadhyay, N. Kumar, Inorg. Nano-met. 47 (10) (2017) 1436–1440.

[20] (a) C.A. Lewis, R. Wolfenden, J. Am. Chem. Soc. 136 (1) (2014) 130–136;
(b) S. Limatibul, J. Watson, J. Org. Chem. 36 (24) (1971) 3805–3807;
(c) R.B. Homer, K.W. Alwis, J. Chem. Soc. Perkin Trans. 2 (1976) 781–784.

[21] (a) L. Rout, S. Jammi, T. Punniyamurthy, Org. Lett. 9 (17) (2007) 3397–3399;
(b) P. Ji, J.H. Atherton, I. Michael, J. Org. Chem. 77 (17) (2012) 7471–7478;
(c) H. Xu, Y. Liang, Z. Cai, H. Qi, C. Yang, Y. Feng, J. Org. Chem. 76 (7) (2011) 2296–2300;
(d) R. Panigrahi, S. Panda, P.K. Behera, Sk. Sahua, L. Rout, New J. Chem. 43 (2019) 19274–19278.