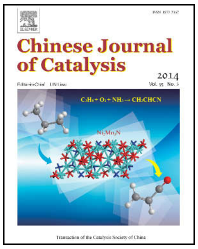
Chinese Journal of Catalysis 35 (2014) 444–450

available at www.sciencedirect.com

ScienceDirect

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



Article

SiO_2-Cu_2O: An efficient and recyclable heterogeneous catalyst for *N*-benzylation of primary and secondary amines

Manjulla Gupta, Satya Paul *, Rajive Gupta

Department of Chemistry, University of Jammu, Jammu-180 006, India

ARTICLE INFO

Article history:
Received 16 September 2013
Accepted 24 December 2013
Published 20 March 2014

Keywords:
Silica supported copper(I) oxide
Benzylation
Substituted amine
Recyclability
Heterogeneous catalysis

ABSTRACT

A mild, effective, and selective procedure is reported for the mono *N*-benzylation and *N*,*N*-dibenzylation of primary amines as well as mono *N*-benzylation of secondary amines using silica-supported copper(I) oxide in water. The silica-supported Cu_2O was generated in situ by the reaction of Fehling solution and glucose at 100 °C onto activated silica. The catalyst was filtered, washed with water, and oven-dried, and was characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, and atomic absorption spectroscopy. The prepared Cu_2O-SiO_2 was found to be thermally stable up to 325 °C. The copper was uniformly distributed onto the surface of the silica, and the mean particle diameter was 7 nm. The catalyst served as a selective heterogenous catalyst for the *N*-benzylation of primary and secondary amines. The catalyst is recyclable and was used effectively upto fifth run without a significant loss of catalytic activity. Various reaction solvents including water, acetonitrile, and toluene were screened for *N*-benzylation of amines, and the success of the aqueous system highlights the low environmental impact of the procedure.

1. Introduction

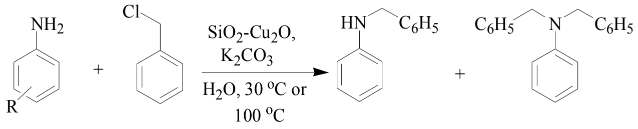
In recent years, there has been growing interest in reactions designed to form carbon–nitrogen bonds, which is a useful strategy in synthetic organic chemistry. In the past few decades, the synthesis of amines has attracted considerable attention because of their industrial and commercial importance [1,2] and also for the synthesis of various dyes. The traditional synthetic approach to *N*-substituted amines is direct *N*-alkylation [3], but this procedure is problematic owing to over-alkylation, the toxic nature of many alkyl halides [4], and poor selectivity [5]. Furthermore, various bases including NaOH [6], cesium hydroxide [7], PhN(n-Pr)$_2$ [8], and Hunig's base [9] have been used for synthesis of *N*-substituted amines, but they require harsh reaction conditions.

Transition metal catalysis has proved useful in selective and atom-economical transformations. Although C–N couplings using palladium [10,11], ruthenium [4], iridium [12,13], and platinum [14,15] catalysts have been explored, copper-catalyzed C–N bond formation has gained more attention because of its low cost, non-toxic nature, and excellent selectivity [16–20]. Heterogenous catalysts have recently gained much importance because they are more selective, stable at high temperature, easily separated from the reaction mixture at the end of the process, and can be reused. These factors favor the cost effectiveness of what can be regarded as a "green reaction". Among the alkylations of amines, benzylation continues to be one of the most commonly used reactions in pharmaceutical chemistry [21,22] because of the medicinal importance of *N*-benzylated amines. Here we report a selective procedure for mono *N*-benzylation and *N*,*N*-dibenzylation of anilines (Scheme 1) and *N*-benzylation of secondary amines (Scheme 2) using

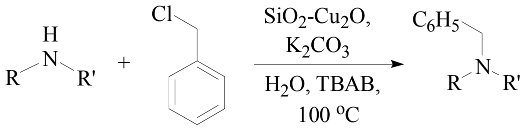
---

* Corresponding author. Tel: +91-191-2453969; Fax: +91-191-2431365; E-mail: paul7@rediffmail.com

DOI: 10.1016/S1872-2067(14)60009-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 3, March 2014



Scheme 1. *N*-Benzylation and *N*,*N*-dibenzylation of amines with benzyl chloride in water.



Scheme 2. *N*-Benzylation of secondary amines with benzyl chloride in water.

silica-supported copper(I) oxide in aqueous media.

2. Experimental

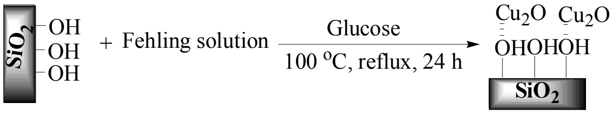
2.1. *Preparation of silica-supported copper(I) oxide (SiO_2-Cu_2O)*

To a round-bottom flask containing activated silica (10 g), Fehling solution (50 mL) was added and the reaction mixture was stirred at 100 °C. After every interval of 30 min, 2 mL of glucose solution (0.5 g in 96 mL of water) was added up to 24 h. Then the catalyst was filtered off, washed with water until the washings were colorless, and dried in an oven at 110 °C. To remove excess glucose, the catalyst was refluxed in water at 120 °C for 6 h (3 × 2 h). Then the catalyst was dried at 110 °C for 5 h in an oven.

The general preparation procedure for silica-supported nano copper(I) oxide (SiO_2-Cu_2O) is shown in Scheme 3.

2.2. *General procedure for mono N-benzylation and N,N-dibenzylation of anilines in the presence of SiO_2-Cu_2O*

A mixture of aniline (0.5 mmol), benzyl chloride (0.5 mmol for mono *N*-benzylation and 2 mmol for *N*,*N*-dibenzylation), K_2CO_3 (0.5 mmol for mono *N*-benzylation and 1 mmol for *N*,*N*-dibenzylation), SiO_2-Cu_2O (0.1 g, 2.5 mol% Cu for mono *N*-benzylation and 0.2 g, 5 mol% Cu for *N*,*N*-dibenzylation), and tetra-*n*-butylammonium bromide (TBAB, 0.082 g, 0.25 mmol, only in the case of *N*,*N*-dibenzylation) in water (5 mL) in a round-bottom flask (50 mL) was stirred at 30 °C for mono *N*-benzylation and 100 °C for *N*,*N*-dibenzylation. On completion of the reaction monitored by thin-layer chromatography (TLC), the reaction mixture was filtered, and the residue was washed with water followed by ethyl acetate (3 × 10 mL). The combined organic extracts were washed with water (3 × 100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was obtained by crystallization from petroleum ether or ethyl acetate/petroleum ether, or by eluting the crude product through a column of silica gel with ethyl acetate/petroleum ether.



Scheme 3. General procedure for the preparation of SiO_2-Cu_2O.

2.3. *General procedure for N-benzylation of secondary amines using SiO_2-Cu_2O*

A mixture of secondary amine (0.5 mmol), benzyl chloride (0.127 g, 1 mmol), K_2CO_3 (0.139 g, 1 mmol), TBAB (0.082 g, 0.25 mmol), and SiO_2-Cu_2O (0.2 g, 5 mol% Cu) in water (5 mL) in a round-bottom flask (50 mL) was stirred at 100 °C. On completion of the reaction (monitored by TLC), the flask was cooled to room temperature and the mixture filtered. The residue was washed with water followed by ethyl acetate (3 × 10 mL). The combined organic extracts were washed with water (3 × 100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was obtained by crystallization from petroleum ether or ethyl acetate/petroleum ether, or by eluting the crude product through a column of silica gel with ethyl acetate/petroleum ether.

2.4. *Selected spectral data*

N-Benzyl-3-methoxyaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 1042 (C–O–C symm. str.), 1582 (aromatic C=C str.), 3029 (aromatic C–H str.), 3422 (NH str.). ^1H NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 4.0 (bs, 1H, NH), 4.33 (s, 2H, CH_2Ph), 6.85–7.0 (m, 4H, Ar–H), 7.16–7.32 (m, 5H, Ar–H). MS: *m*/*z* 213 (M^+).

N-Benzyl-4-methylaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 1575 (aromatic C=C str.), 2918 (C–H str.), 3021 (aromatic C–H str.), 3427 (N–H str.). ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H, CH_3), 4.02 (bs, 1H, NH), 4.37 (s, 2H, CH_2Ph), 6.86–6.96 (d, 2H, Ar–H), 7.06–7.17 (d, 2H, Ar–H), 7.33–7.46 (m, 5H, Ar–H). MS: *m*/*z* 197 (M^+).

N-Benzyl-4-chloroaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 740 (C–Cl str.), 1580 (aromatic C=C str.), 3029 (aromatic C–H str.), 3420 (N–H str.). ^1H NMR ($CDCl_3$): δ 4.13 (bs, 1H, NH), 4.29 (s, 2H, CH_2Ph), 6.89–6.97 (d, 2H, Ar–H), 7.21–7.34 (m, 5H, Ar–H), 7.50–7.58 (d, 2H, Ar–H). MS: *m*/*z* 217 (M^+), 219 (M+2).

N-Benzyl-4-nitroaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 865 (C–NO_2 str.), 1530 (NO_2 str.), 1585 (aromatic C=C str.), 3039 (aromatic C–H str.), 3460 (N–H str.). ^1H NMR ($CDCl_3$): δ 4.10 (bs, 1H, NH), 4.25 (s, 2H, CH_2Ph), 6.94–7.03 (d, 2H, Ar–H), 7.46–7.59 (m, 5H, Ar–H), 8.01–8.12 (d, 2H, Ar–H). MS: *m*/*z* 228 (M^+).

N,*N*-Dibenzyl-3-methoxyaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 1052 (C–O–C symm. str.), 1579 (aromatic C=C str.), 3029 (aromatic C–H str.). ^1H NMR ($CDCl_3$): δ 3.83 (s, 3H, OCH_3), 4.35 (s, 4H, 2 × CH_2Ph), 6.87–7.20 (m, 4H, Ar–H), 7.29–7.34 (m, 10H, Ar–H). MS: *m*/*z* 303 (M^+).

N,*N*-Dibenzyl-4-methylaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 1572 (aromatic C=C str.), 2925 (C–H str.), 3017 (aromatic C–H str.). ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 4.42 (s, 4H, 2 × CH_2Ph), 6.89–6.97 (d, 2H, Ar–H), 7.08–7.18 (d, 2H, Ar–H), 7.29–7.46 (m, 10H, Ar–H). MS: *m*/*z* 287 (M^+).

N,*N*-Dibenzyl-4-chloroaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 743 (C–Cl str.), 1582 (aromatic C=C str.), 3030 (aromatic C–H str.), 3422 (N–H str.). ^1H NMR ($CDCl_3$): δ 4.13 (s, 4H, 2 × CH_2Ph), 6.93–7.02 (d, 2H, Ar–H), 7.25–7.40 (m, 10H, Ar–H), 7.48–7.57 (d, 2H, Ar–H). MS: m/z 307 (M$^+$), 309 (M+2).

N,*N*-Dibenzyl-3-nitroaniline (Table 3). IR (υ_{max} in cm^{-1}, KBr): 860 (C–NO_2 str.), 1530 (NO_2 str.), 1585 (aromatic C=C str.), 3047 (aromatic C–H str.). ^{1}H NMR ($CDCl_3$): δ 4.33 (s, 4H, 2 × CH_2Ph), 7.13–7.21 (m, 2H, Ar–H), 7.53–7.63 (m, 10H, Ar–H), 8.16–8.27 (m, 2H, Ar–H). MS: m/z 318 (M$^+$).

N-Benzylmorpholine (Entry 1, Table 4). IR (υ_{max} in cm^{-1}, KBr): 1050 (C–O–C str.), 1340 (C–N str.), 1565 (C=C aromatic str.), 3070 (C–H symm. str.). ^{1}H NMR ($CDCl_3$): δ 2.43 (t, 4H, CH_2), 4.92 (s, 2H, CH_2Ph), 3.70 (t, 4H, CH_2), 7.04–7.16 (m, 5H, Ar–H). MS: m/z 177 (M$^+$).

N-Benzylpiperidine (Entry 2, Table 4). IR (υ_{max} in cm^{-1}, KBr): 1310 (C–N str.), 1560 (C=C aromatic str.), 3085 (C–H aromatic str.). ^{1}H NMR ($CDCl_3$): δ 1.40 (m, 6H, CH_2), 2.24 (m, 4H, CH_2), 4.90 (s, 2H, CH_2Ph), 7.12–7.23 (m, 5H, Ar–H). MS: m/z 175 (M$^+$).

3. Results and discussion

3.1. *Characterization of SiO_2-Cu_2O*

Prepared SiO_2-Cu_2O was characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic absorption spectroscopy (AAS). In the FTIR spectra, the activated silica showed absorption peaks at 459, 800, 964, 1344, 1384, 1400, 1598, 2341, 2362, 2856, and 2929 cm^{-1}, and wide absorption bands were observed at 1078 and 3396 cm^{-1} (Fig. 1). For SiO_2-Cu_2O, an additional peak observed at 669 cm^{-1} was attributed to Cu_2O (Fig. 2).

The stability of the SiO_2-Cu_2O was determined by TGA (Fig. 3). The curve showed an initial weight loss up to 116 °C, which was attributed to the loss of residual water trapped onto the surface of the silica. This was followed by a slight weight loss up to 325 °C, which was considered to be caused by the loss of unreacted glucose or components of Fehling solution. Further continuous weight loss occurred up to 648 °C. This indicates that the catalyst is stable up to 325 °C and is safe to use in reactions at 100 °C.

The XRD diffraction patterns for SiO_2-Cu_2O showed peaks that were indexed on the basis of crystallographic data for the known structure of silica. In addition, reflection patterns were found corresponding to 2θ = 36.3° and 42.2°, which were attributed to Cu_2O. The absence of a peak at 2θ = 38.7° excluded the possibility of CuO formation (Fig. 4).

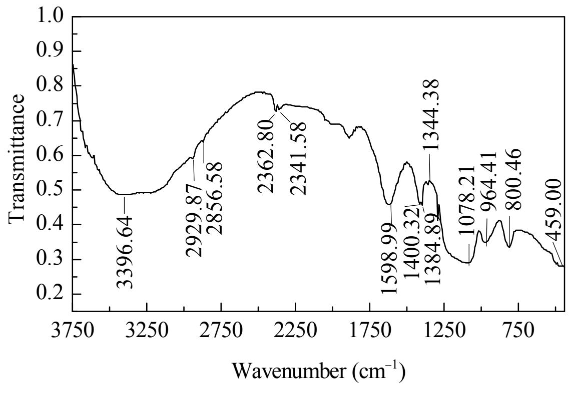


Fig. 1. FTIR spectrum of activated silica.

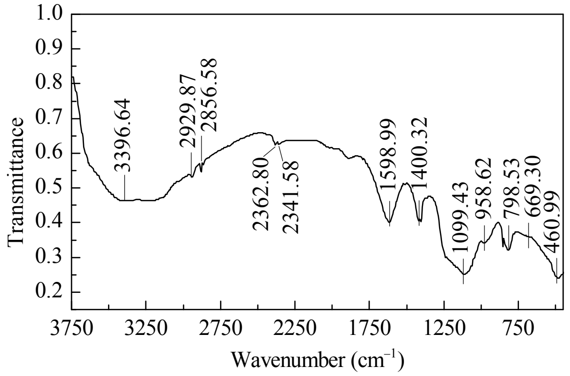


Fig. 2. FTIR spectrum of SiO_2-Cu_2O.

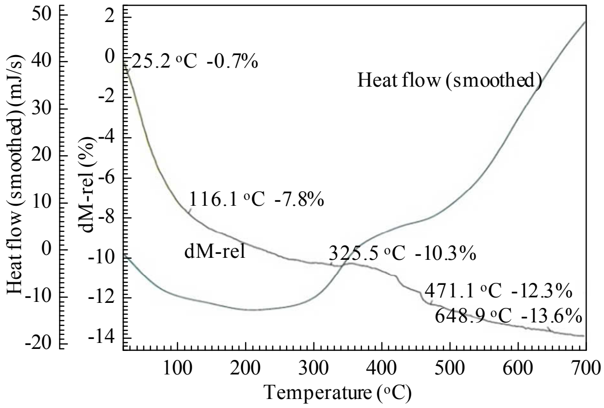


Fig. 3. TGA of SiO_2-Cu_2O.

The oxidation state of copper in the SiO_2-Cu_2O was determined by measurements of binding energies using XPS. The spectrum of Cu 2$p_{3/2}$ photoelectrons is shown in Fig. 5. The intense and broad peak at 933 eV corresponds to Cu(I) and is in accordance with the literature values [23,24].

The amount of copper loaded onto the silica surface was determined by AAS analysis. The catalyst was stirred in dilute HNO_3 solution and then subjected to AAS analysis. The SiO_2-Cu_2O contained 0.0158 g of copper per gram of catalyst. The microstructure and morphology of the SiO_2-Cu_2O was studied by SEM and TEM. The SEM image revealed a fine ho-

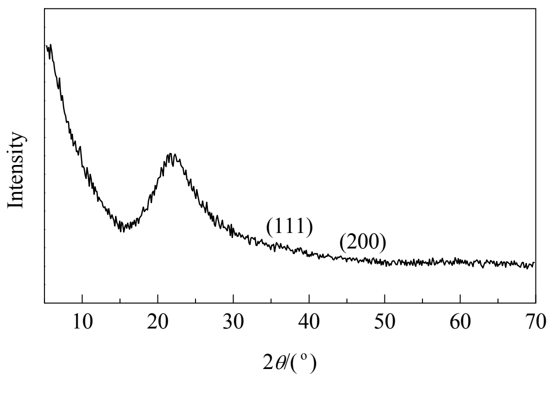


Fig. 4. XRD pattern of SiO_2-Cu_2O.

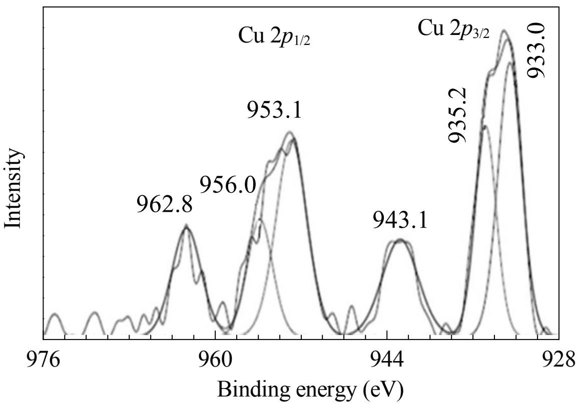


Fig. 5. XPS spectra of SiO_2-Cu_2O.

mogenous powder with a porous structure (Fig. 6).

The TEM micrographs of the catalyst showed that copper was uniformly distributed on the surface of silica (Fig. 7). The mean particle diameter was found to be 7 nm. Furthermore, no bulk aggregation of the metal was observed, indicating that the copper was evenly dispersed onto the surface of the silica.

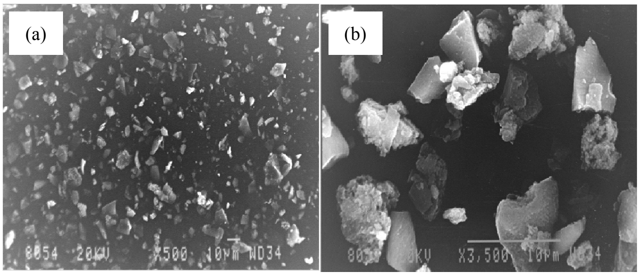


Fig. 6. SEM images of SiO_2-Cu_2O. (a) × 500; (b) × 3500.

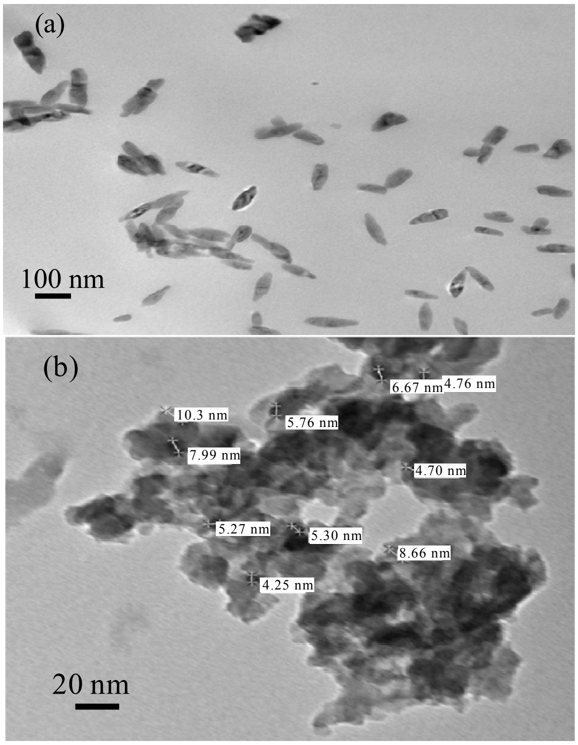


Fig. 7. TEM images of SiO_2-Cu_2O.

Table 1
Effect of solvent on the SiO_2-Cu_2O catalyzed *N*-benzylation of 4-nitroaniline in water.

Solvent	Yield [a] (%)
Acetonitrile	90
Toluene [b]	60
Water	95

Reaction conditions: 4-nitroaniline (0.069 g, 0.5 mmol), benzyl chloride (0.0635 g, 0.5 mmol), SiO_2-Cu_2O (0.1 g, 2.5 mol% Cu), K_2CO_3 (0.069 g, 0.5 mmol), solvent (5 mL), 30 °C, 8 h, air atmosphere.
[a] Based on separation by column chromatography.
[b] Along with *N*-benzyl-4-nitroaniline, *N*,*N*-dibenzyl-4-nitroaniline was also formed together with unreacted amine.

3.2. Catalyst testing for selective N-benzylation of primary and secondary amines

The reaction conditions for selective mono *N*-benzylation were optimized by using 4-nitroaniline as the test substrate and benzyl chloride as the benzylating agent. The reaction was carried out under different conditions with respect to solvent, temperature, and molar ratios of SiO_2-Cu_2O. After carrying out a series of reactions, 2.5 mol% of Cu in SiO_2-Cu_2O was found to be sufficient to complete the reaction selectively and give maximum yield of *N*-benzyl-4-nitroaniline. Solvents of different polarities were also tried, and the results are presented in Table 1.

The best results were obtained when water was used as solvent, with consideration to environmental impact, reaction time, yield, and selectivity. The reaction temperature also plays a crucial role in the *N*-benzylation of anilines; therefore, the reaction of the test substrate was also conducted at different temperatures, and the yield of mono *N*-benzyl-4-nitroaniline was determined (Table 2).

For *N*,*N*-dibenzylation, 4-chloroaniline was selected as the test substrate, and benzyl chloride was used as the benzylating agent. At room temperature, no dibenzylated product was formed, so the reaction temperature was increased to 100 °C. The dibenzylated product formed as the major product with a small amount of mono benzylated product. Further addition of TBAB increased the amount of dibenzylated product. With 4-toluidine, 2-toluidine, 4-chloroaniline, or 4-bromoaniline as the substrates, the *N*,*N*-dibenzylated product was formed exclusively. However, for 2-chloroaniline and 2-nitroaniline, only the *N*-benzylated product was formed, and no *N*,*N*-dibenzylated

Table 2
Effect of temperature on the SiO_2-Cu_2O catalyzed *N*-benzylation of 4-nitroaniline in water.

Temperature (°C)	Yield [a] (%)	
	Mono	Di
30	95	0
40	80	10
60	75	12
80	40	35
100	30	50

Reaction conditions: 4-nitroaniline (0.069 g, 0.5 mmol), benzyl chloride (0.0635 g, 0.5 mmol), SiO_2-Cu_2O (0.1 g, 2.5 mol% Cu), K_2CO_3 (0.069 g, 0.5 mmol), H_2O (5 mL), 8 h, air atmosphere.
[a] Based on separation by column chromatography.

Table 3

SiO_2-Cu_2O catalyzed selective *N*-benzylation and *N,N*-dibenzylation of anilines in water.

Entry	Amine	*N*-Benzylation of anilines[a]			*N,N*-Dibenzylation of anilines[b]		
		Yield[c] (%)	Time (h)	MP or BP/Ref. (°C)	Yield[c] (%)	Time (h)	MP or BP/Ref. (°C)
		Amine/Mono/Di			Di/Mono		
1	3-Anisidine	40/50/0	5	Liq/183–187 [25]	80/14	17	55–56/56 [32]
2	2-Anisidine	15/78/0	1.5	Oil/oil [26]	—	—	—
3	4-Toluidine	15/75/5	4	243–245/244–245 [27]	97/0	10	62–63/63–64 [33]
4	3-Toluidine	15/55/10	15	166–168/160–170 [28]	82/11	17	74–75/75–76 [34]
5	2-Toluidine	—	—	—	97/0	9	42–43/42 [35]
6	4-Fluoroaniline	0/60/30	4	36–38/38–39 [29]	—	—	—
7	4-Chloroaniline	0/80/10	3	46–47/46–48 [30]	96/0	11	104–106/104–105 [36]
8	2-Chloroaniline[d]	20/75/0	12	38–40/38–39 [26]	0/96	1.5	38–39/38–39 [31]
9	4-Bromoaniline	10/82/0	0.75	50–51/51–52 [30]	93/0	16	124–125/124–126 [37]
10	4-Nitroaniline	0/95/0	8	73–74/72–74 [31]	65/20	17	86–87/84–86 [32]
11	3-Nitroaniline	20/70/0	10	104–106/106–107 [29]	80/10	16	73–75/73–74 [38]
12	2-Nitroaniline	—	—	—	0/95	18	65–66/66–67 [39]

[a] Reaction conditions: amine (0.5 mmol), benzyl chloride (0.0635 g, 0.5 mmol), SiO_2-Cu_2O (0.1 g, 2.5 mol% Cu), K_2CO_3 (0.069 g, 0.5 mmol), H_2O (5 mL), 30 °C.

[b] Reaction conditions: amine (0.5 mmol), benzyl chloride (0.254 g, 2 mmol), TBAB (0.082 g, 0.25 mmol), K_2CO_3 (0.139 g, 1 mmol), SiO_2-Cu_2O (0.2 g, 5 mol % Cu), water (5 mL), 100 °C.

[c] Isolated yield based on separation through column chromatography or crystallization.

[d] Benzyl chloride (0.127 g, 1 mmol) was used for for *N,N*-dibenzylation of anilines.

product was observed. For *N*-benzylation of secondary amines, morpholine was used as the test substrate and benzyl chloride as the benzylating agent. After carrying out a series of reactions, 5 mol% of Cu in SiO_2-Cu_2O was found to be sufficient to achieve good yields. Being benign and environmentally friendly, water was used as the solvent. Furthermore, the addition of base was found to have a profound effect on the rate of the reaction. Various bases were screened for the test reaction, and K_2CO_3 was selected because of its wide availability and low cost. A reaction temperature of 100 °C was found to be the optimum reaction temperature. Addition of TBAB as phase transfer catalyst was also found to enhance the reaction rate.

To study the generality of the developed protocol for mono *N*-benzylation and *N,N*-dibenzylation, various anilines substituted with electron-withdrawing and electron-releasing groups were chosen. The results are presented in Table 3. For *N*-benzylation of secondary amines, various secondary amines were chosen and products were obtained in almost quantitative yields (Table 4). To confirm the role of the catalyst for *N*-benzylation of primary and secondary amines, the test reaction was also carried out with the test substrate in the absence of catalyst. The reaction was observed to proceed very slowly in the absence of catalyst, confirming the catalytic effect of SiO_2-Cu_2O.

Table 4

SiO_2-Cu_2O catalyzed *N*-benzylation of secondary amines in water at 100 °C.

Entry	Amine	Time (h)	Yield[a] (%)	MP/Ref. (°C)
1	Morpholine	0.5	93	194–195/194 [40]
2	Piperidine	0.5	90	182–183/181–182 [41]
3	Diphenylamine[b]	12	80	85–87/86–87 [42]
4	Imidazole[c]	12	80	70–72/71–73 [43]

Reaction conditions: amine (0.5 mmol), benzyl chloride (0.127 g, 1 mmol), K_2CO_3 (0.139 g, 1 mmol), TBAB (0.082 g, 0.25 mmol), SiO_2-Cu_2O (0.2 g, 5 mol% Cu), water (5 mL), 100 °C.

[a] Isolated yield.

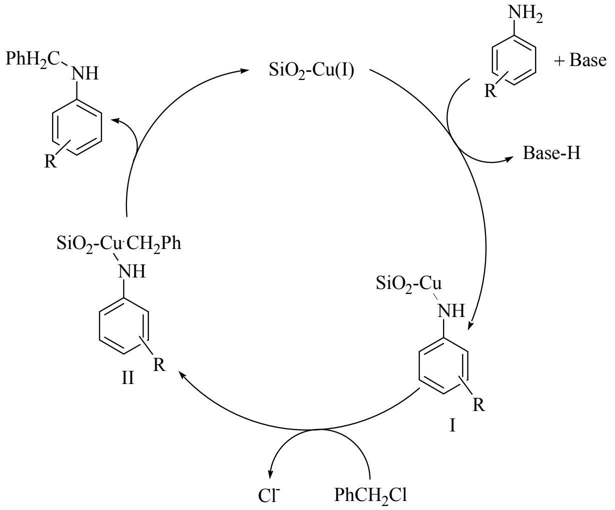
[b] Rest being the starting material.

[c] Product was obtained after passing through column of silica gel and elution with ethyl acetate/petroleum ether.

The mechanism for the *N*-benzylation of amines catalyzed by SiO_2-Cu_2O is considered to proceed through a recyclable coordination process via oxidative addition followed by reductive elimination (Scheme 4). First, the oxidative addition of amine to copper is thought to occur in the presence of base to give a copper complex (**I**), followed by the addition of benzyl chloride to form the second intermediate (**II**). Intermediate **II** then undergoes reductive elimination to give the product.

3.3. Recyclability of SiO_2-Cu_2O for N-benzylation of amines

In the use of heterogeneous catalysts, the recyclability of the catalyst is an important factor. To determine the recyclability, a



Scheme 4. Proposed mechanism for *N*-benzylation of amines using SiO_2-Cu_2O.

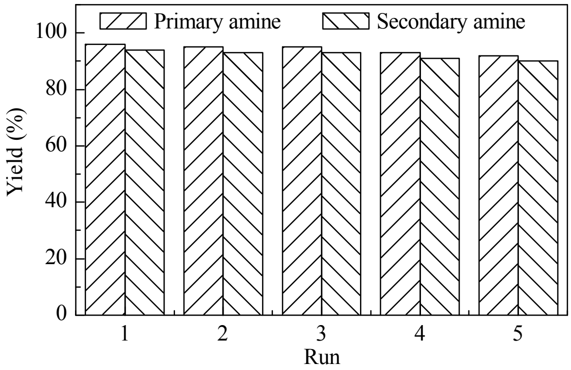


Fig. 8. Recyclability of SiO_2-Cu_2O. Reaction conditions for primary amine: 2-chloroaniline (0.5 mmol), benzyl chloride (0.127 g, 1 mmol), TBAB (0.082 g, 0.25 mmol), K_2CO_3 (0.139 g, 1 mmol), SiO_2-Cu_2O (0.2 g, 5 mol% Cu), water (5 mL), 100 °C. Reaction conditions for secondary amine: morpholine (0.5 mmol), benzyl chloride (0.127 g, 1 mmol), K_2CO_3 (0.139 g, 1 mmol), TBAB (0.082 g, 0.25 mmol), SiO_2-Cu_2O (0.2 g, 5 mol% Cu), water (5 mL), 100 °C.

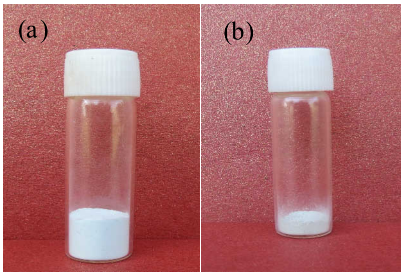


Fig. 9. (a) Freshly prepared SiO_2-Cu_2O; (b) SiO_2-Cu_2O after 5th use.

series of five consecutive runs were carried out (reactions of entry 8, Table 3 and entry 1, Table 4). Almost no change was observed in the catalyst activity after the fifth use (Fig. 8).

The catalyst after fifth use showed the presence of Cu(II), as indicated by magnetic moment measurements. A comparison of the fresh catalyst and that after a fifth use is shown in Fig. 9.

4. Conclusions

We have prepared an efficient and recyclable silica-supported copper(I) oxide catalyst and studied its application for the selective mono *N*-benzylation and *N*,*N*-dibenzylation of primary aromatic amines. The catalytic system has also been used for the *N*-benzylation of secondary amines. The environmentally friendly nature of the reaction is underscored by the use of water as the reaction solvent.

Acknowledgements

We are grateful to Director, SAIF, Punjab University, Chandigarh for SEM, TEM, and XRD and also extend our sincere thanks to UGC, New Delhi for financial support to purchase FTIR; awarding Major Research Project (F 41-281/2012 (SR)), and Prof. R. K. Bamezai, Department of Chemistry, University of Jammu for recording TGA.

References

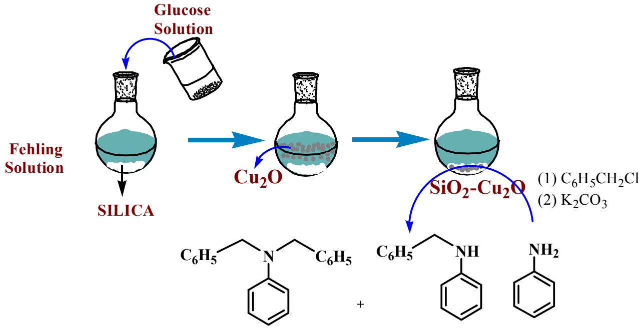
[1] Ju Y, Varma R S. *Green Chem*, 2004, 6: 219
[2] Wells J M, Harvey J M. *Phytopathology*, 1970, 60: 116
[3] Salvatore R N, Yoon C H, Jung K W. *Tetrahedron*, 2001, 57: 7785
[4] Haniti M, Hamid S A, Allen C L, Lamb G W, Maxwell A C, Maytum H C, Watson A J A, Williams J M J. *J Am Chem Soc*, 2009, 131: 1766
[5] Bolm C, Fey T. *Chem Commun*, 1999: 1795
[6] O' Meara J A, Gardee N, Jung M, Ben R N, Durst T. *J Org Chem*, 1998, 63: 3117
[7] Salvatore R N, Nagle A S, Schmidt S E, Jung K W. *Org Lett*, 1999, 1: 1893
[8] Sommer H Z, Lipp H I, Jackson L L. *J Org Chem*, 1971, 36: 824
[9] Moore J L, Taylor S M, Soloshonok V A. *ARKIVOC*, 2005, (vi): 287
[10] Harris M C, Geis O, Buchwald S L. *J Org Chem*, 1999, 64: 6019
[11] Artamkina G A, Ermolina M V, Beletskaya I P. *Mendeleev Commun*, 2003, 13: 158
[12] Fujita K I, Li Z, Ozeki N, Yamaguchi R. *Tetrahedron Lett*, 2003, 44: 2687
[13] Li J Q, Andersson P G. *Chem Commun*, 2013, 49: 6131
[14] Yin M Y, He S B, Yu Z K, Wu K K, Wang L D, Sun C L. *Chin J Catal*, 2013, 34: 1534
[15] He W, He S B, Sun C L, Wu K K, Wang L D, Yu Z K. *Chin J Catal*, 2012, 33: 717
[16] Xu H, Wolf C. *Chem Commun*, 2009: 3035
[17] Wang D P, Ding K. *Chem Commun*, 2009: 1891
[18] Xu H, Wolff C. *Chem Commun*, 2009: 1715
[19] Phan N T S, Brown D H, Styring P. *Green Chem*, 2004, 6: 526

Graphical Abstract

Chin. J. Catal., 2014, 35: 444–450 doi: 10.1016/S1872-2067(14)60009-7

SiO_2-Cu_2O: An efficient and recyclable heterogeneous catalyst for *N*-benzylation of primary and secondary amines

Manjulla Gupta, Satya Paul*, Rajive Gupta
University of Jammu, India



Silica-supported Cu_2O was prepared in situ using inexpensive and widely available starting materials and used as a catalyst for *N*-benzylation and *N*,*N*-dibenzylation of primary and secondary amines.

[20] Sharma R K, Monga Y, Puri A, Gaba G. *Green Chem*, 2013, 15: 2800

[21] Dolle R E, Bourdonnec B L, Goodman A J, Morales G A, Thomas C J, Zhang W. *J Comb Chem*, 2009, 11: 739

[22] Fenster E, Rayabarapu D K, Zhang M, Mukherjee S, Hill D, Neuenswander B, Schoenen F, Hanson P R, Aube J. *J Comb Chem*, 2008, 10: 230

[23] Auroux A, Gervasini A, Guimon C. *J Phys Chem B*, 1999, 103: 7195

[24] Zhang H R, Shen C M, Chen S T, Xu Z C, Liu F S, Li J Q, Gao H J. *Nanotechnology*, 2005, 16: 267

[25] Horlein, Ulrich. *Chem Ber*, 1954, 87: 463

[26] Kumar K A, Sreelekha T S, Shivakumara K N, Prakasha K C, Gowda D C. *Synth Commun*, 2009, 39: 1332

[27] Dahn H, Zoller P. *Helv Chim Acta*, 1952, 35: 1348

[28] Grunfeld, Maximilien. *Bull Soc Chim Fr*, 1937, 4: 654

[29] Moldt P, Ostergaard N E. US Patent 5296493. 1994

[30] Roe A, Montgomery J A. *J Am Chem Soc*, 1953, 75: 910

[31] Hayat S, Atta-ur-Rahman, Choudhary M I, Khan K M, Schumann W, Bayer E. *Tetrahedron*, 2001, 57: 9951

[32] Benkeser R A, DeBoer C E. *J Org Chem*, 1956, 21: 281

[33] Menche D, Arikan F, Li J, Rudolph S, Sasse F. *Bioorg Med Chem*, 2007, 15: 7311

[34] Florvall L, Fagerwall I, Ask A L, Ross S B. *J Med Chem*, 1986, 29: 2250

[35] Courtot Ch, Petitcolas P. *Bull Soc Chim Fr*, 1926, 39: 452

[36] Leoppky R N, Tomasik W. *J Org Chem*, 1983, 48: 2751

[37] Saitoh T, Ichikawa J. *J Am Chem Soc*, 2005, 127: 9696

[38] Weaver M A, Pridgen H S. US Patent 3765830. 1973

[39] Kruse L I, Kaiser C, DeWolf W E, Finkelstein J A, Frazee J S, Hilbert E L, Ross S T, Flaim K E, Sawyer J L. *J Med Chem*, 1990, 33: 781

[40] Kyrides L P, Meyer F C, Zienty F B, Harvey J, Bannister L W. *J Am Chem Soc*, 1950, 72: 745

[41] Lukasiewicz A. *Tetrahedron*, 1963, 19: 1789

[42] Liu Z, Larock R C. *J Org Chem*, 2006, 71: 3198

[43] Jayaram P N, Roy G, Mugesh G. *J Chem Sci*, 2008, 120: 143