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Self-coupling of benzylamines over a highly active and selective supported copper catalyst to produce N-substituted amines by the borrowing hydrogen method

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ABSTRACT

Amines were used as hydrogen donor for the borrowing hydrogen methodology with a heterogeneous catalyst. Supported copper catalysts catalyzed the self-condensation reaction of primary amines to secondary amines/imines with high efficiency. The recyclable, non-leaching catalyst is synthesized by a sol–gel method, which allows entrapping copper nanoparticles in an alumina matrix. The synthesized copper catalysts were found to be active in the self-coupling of primary amines to produce secondary amines. The hydrogen donor for the transfer hydrogenation appears to be the primary amine, and no additional hydrogen or hydrogen transfer reagent is required. To the best of our knowledge, this is the first report of a copper based catalyst for this type of reaction using the borrowing hydrogen scheme.

1. Introduction

N-alkylation of amines to produce secondary amines is classically carried out through a S_N2 mechanism using alkyl halides or aliphatic compounds having other good leaving groups [1]. The conventional method suffers from many drawbacks such as low atom efficiency, production of waste and by-products, and low selectivity toward the desired secondary amines because of the competing formation of undesired tertiary amines and alkyl ammonium halides. These drawbacks are avoided if the amine itself is the alkylation agent using a reaction sequence that has been variously termed ‘hydrogen autotransfer’, ‘borrowing hydrogen mechanism’ or ‘self-supply system for active hydrogen’ [2–4]. This process uses normally alcohols, but amines can also act as the electrophiles (Scheme 1) in this process. The catalyst “borrows” a molecule of hydrogen when the reactive species (aldehyde or imine) is formed and subsequently “auto transfers” it to the unsaturated intermediate to form the final product. With alcohols as the initial source of the electrophile, this reaction sequence can be initialized by several catalysts such as Pd [5], Pt [6], Ru [7], Ir [8], Ag [9], Au [10] and CuAg bimetallic catalysts [11]. The same methodology has also been applied for N-alkylation of nitroaromatics [12], N-alkylation of amines [5,7,9,10], transamidation of carboxyamides and ureas [13], and C—C bond formation [14]. Compared to the use of alcohols as the source of electrophiles, the alkylation of amines with other amines is much less developed.

Instead of alcohols, amines can also serve as alkylating agent, and the oxidative coupling of a primary amine to the corresponding secondary imine and water has recently been reported over graphite oxide (GO) [15] and Cu-based catalysts [13]. However, the one-pot transformation of primary amines to secondary amines with return of the ‘borrowed’ hydrogen is still a challenge. Corma’s [16] group reported a supported gold catalysts (Au/TiO_2) which catalyzed the aerobic oxidative condensation of benzylamines to secondary imines and described the hydrogenation of this imine to the secondary amine in a one-pot, two-step process. Even though high yields (98% of dibenzylamine) could be obtained, two steps involving charging of O_2 (5 bar) and H_2 (7 bar) separately to the reaction vessel are required.

Several attempts of the N-alkylation of amines with other amines as electrophiles over homogeneous catalysts have been described. Ruthenium complexes [16–18] were the most successful catalysts to perform this hydrogen autotransfer process using amines as electrophiles. Beller’s group [17] reported a procedure for the synthesis of secondary amines from the amines using the commercial Shvo and Shvo-H_2 complex. They achieved the arylation of aliphatic amines with anilines under transfer

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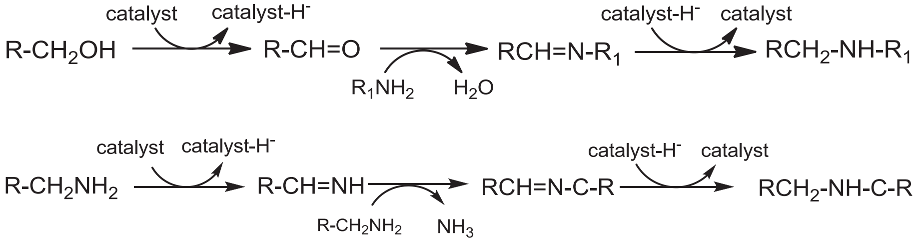


Scheme 1. (a) Hydrogen autotransfer process for alcohols as electrophiles (top) and (b) hydrogen autotransfer process for amines as electrophiles (below).

hydrogenation conditions in moderate to high yield (20–99%). Besides ruthenium based homogeneous catalysts, $Os_3(CO)_{12}$ [19] is another transition-metal complex which was able to catalyze the alkylation of amines with other amines. However, only a low yield (<30%) to the secondary amine was obtained at 150 °C under 7 atm nitrogen pressure. The Ir-based catalyst, ($IrCl_2Cp*$(NHC)), recently reported by Peris' group [20], was found to be active in the N-alkylation of anilines with aliphatic amines. However, homogeneous systems have disadvantages including the difficulties in the recovery and reuse of the expensive catalysts and the requirement for co-catalysts such as bases and stabilizing ligands.

Compared to homogeneous catalysts, much less work has been done with heterogeneous catalysts for the alkylation of amines using the amine as an electrophile. Historically, nickel was the first metal catalyst used to perform the N-alkylation of amines with other amines as the source of electrophiles. Initially, heterogeneous catalysts were used in other processes such as the selective nitrile hydrogenation where the N-alkylation of amines by other amines was observed as an unwanted side reaction. However, later this reaction gained the attention of the scientific community. During nitrile hydrogenation to obtain primary amines, symmetrical secondary amines were formed in low yields (2–47%). This reaction was performed at 20 atm of hydrogen and 110–130 °C in tetralin or decalin [21]. A copper-chromite catalyst ($CuCr_2O_4$–$BaCr_2O_4$ 93 mol%) was reported for the synthesis of the symmetrical secondary amine dilaurylamine (didodecylamine) by hydrogenation of lauramide at 220 °C under 340–365 atm of hydrogen pressure, and didodecylamine was obtained in moderate yield (52%) [22]. Processes involving amines as the electrophiles were also reported over Pd [23–25] and Pt [26,27] based catalysts. When benzyl amine was treated with palladium black (5 mol%) at 80 °C, 41% of dibenzylamine was formed after 12 h, together with 41% of the corresponding imine [23]. Shimizu's group [27] reported that alumina-supported Pt nanoclusters with average size of 0.8 nm were an effective catalyst for mono-N-alkylation of amines with various amines. $(iPr)_2NH$ was identified to be a good source of electrophiles to convert various amines to N-isopropyl derivatives and give high yields (70–96%). In a subsequent publication, the same authors showed that alumina-supported Pd with an average Pd cluster size of 1.8 nm was a highly effective catalyst for N-alkylation of benzylamines with cyclic secondary amines [24]. Under the conditions of the reaction, the self cross coupling product, dibenzylamine, was also formed as an important by-product with a yield of 4–26%. Coordinatively unsaturated Pd atoms were found to be necessary for good activity in this sterically demanding reaction.

We have described a procedure for the synthesis of secondary amines starting from the corresponding primary amines or nitroarenes using Ag/Al_2O_3 catalysts [9]. Using this method, we successfully achieved the N-alkylation of amines with different alcohols as the electrophile. Here, we present a new methodology for the synthesis of secondary amines following a similar scheme. In analogy to the amination of alcohols, the reaction occurs through a hydrogen-borrowing mechanism. The hydrogen autotransfer process of amine alkylation begins with the oxidation/dehydrogenation of an alkylamine to the corresponding imine (iminium). This is followed by the addition of a second nucleophilic amine to the *in situ* formed imine, generating an aminal intermediate, elimination of the initial dealkylated amine, and formation of a new imine (iminium), with a final hydrogenation of this imine [17]. The thermodynamics of the whole process are in some cases highly favorable [28], particularly when ammonia is one of the products of the reactions (Scheme 1b). In this reaction, the hydrogen donor for the transfer hydrogenation is the primary amine. Hence, no additional hydrogen or hydrogen transfer reagent is required. The advantage of this method compared to most reductive aminations is the high atom efficiency and the fact that no high-pressure equipment is required [29]. In this paper, we describe our results with various copper and silver catalysts. Copper catalysts were found to be particularly active for the self coupling of amines to secondary amines. To the best of our knowledge, this is the first reported copper based heterogeneous catalyst for this type of reaction using the borrowing hydrogen scheme.

2. Experimental

2.1. Synthesis of Cu/Al_2O_3 catalysts

In a typical synthesis for a 5 wt% Cu/Al_2O_3 sample, copper acetate monohydrate (312 mg/1.56 mmol), aluminum tri-*sec*-butoxide (9.54 ml/37.2 mmol) and 2-butanol (2 ml) were added together. The resulting gel was stirred at 100 °C for 3 h to give a light blue suspension, following the dropwise addition of deionized water (4.5 ml). After stirring for another hour at 100 °C, the suspension was cooled to room temperature and filtered. The solid catalyst was washed with acetone, dried at 100 °C and calcined for 1 h at 600 °C (10 °C/min ramp). Prior to use, the catalyst was activated in flowing H_2 at 300 °C for 60 min. The metal content was determined by ICP-AES.

Several other 5 wt% Cu samples were prepared for comparison by means of a conventional wet impregnation method. Various supports were used, including commercially available γ-Al_2O_3 (Merck). These samples were prepared by slurrying 0.95 g of the support with 15 ml of an aqueous solution of copper acetate monohydrate (0.157 g). The suspension was stirred for 4 h at room temperature before increasing the temperature to 90 °C to evaporate the water. The slightly wet residue was left to dry overnight at 100 °C before calcination for 1 h at 600 °C and activation in flowing H_2 at 300 °C for 60 min.

2.2. Procedure for self-coupling of amine

The catalytic self-coupling of benzyl amine was carried out under 1 atm He at 150 °C in a 22 ml glass liner inside an autoclave. Typically, 2 mmol of amine was dissolved in 5 ml p-xylene and 0.150 g catalyst was added. The autoclave with the reaction mixture was purged with He three times and then filled with 1 atm

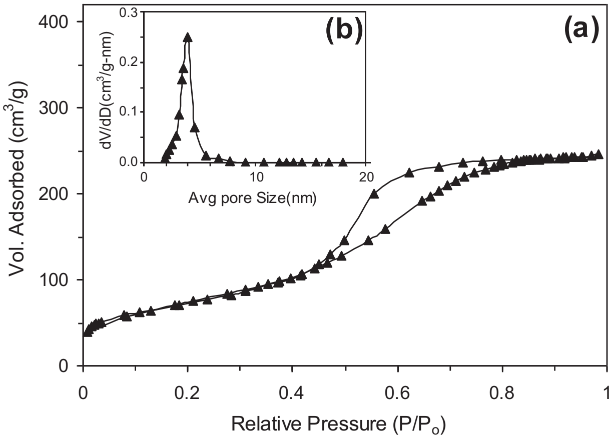


Fig. 1. (a) N_2 adsorption isotherm of 5 wt% Cu/Al_2O_3 and (b) the corresponding pore size distribution.

He before the reaction was carried out. After 24 h, the reaction was stopped and the autoclave was cooled to room temperature. After opening, the residual liquid was subjected to analysis by GC. The products were identified by GC–MS.

3. Results and discussions

3.1. Textural properties

The textural properties of the catalysts tested are listed in Table S1. The surface area depends mainly on the carrier material and the preparation method. The Cu/Al_2O_3 samples prepared by *in-situ* generation of the support have high surface areas in excess of 250 m^2/g after calcination at 600 °C for 1 h. The 5 wt% Cu/Al_2O_3 has a surface area of 268 m^2/g, which is almost twice that of material prepared by wet impregnation onto γ-Al_2O_3 (122 m^2/g). The N_2-sorption isotherms of 5 wt% Cu/Al_2O_3 sample exhibit typical type IV isotherms (Fig. 1a) with a hysteresis loop at $P/P_o \sim 0.4$–0.8, indicative of the presence of mesopores in the structure. The highly porous nature of the samples is seen in the large pore volume of 0.381 cm^3/g for 5 wt% Cu/Al_2O_3 (Fig. 1b) with average pore size ~4 nm. The X-ray powder diffractograms of samples with 5 wt% Cu/Al_2O_3 prepared by the sol–gel *in situ* synthesis method showed only the broad peaks of the γ-Al_2O_3 support (Fig. S1). The absence of reflexes due to Cu suggests that the metal is well dispersed on the support so that the crystallite size of the Cu nanoparticles is below the detection limit of X-ray diffractometry, which is about 4 nm.

The oxidation state of the Cu species is obtained from the X-ray photoelectron spectrum (XPS). The binding energies for the Cu $2p_{3/2}$ photoelectron transitions and the satellite peak were determined to be 290.1 eV and 940.6 eV (Fig. S2 in the Supplementary Material). The XPS results clearly indicate the presence of CuO for the 5 wt% Cu/Al_2O_3 catalyst because the weak and diffuse Cu $2p_{3/2}$ satellite peak due to shake-up transitions by ligand-to-metal 3d charge transfer only occurs on CuO. This type of charge transfer cannot take place in Cu_2O or Cu as they both have completely filled 3d orbitals. However, the presence of CuO on the surface is easily explained by the exposure of the reduced samples to air at room temperature when the samples were prepared for XPS analysis.

The TEM image (Fig. 2) of the 5 wt% Cu/Al_2O_3 reveals the fibrous nature of the support which is typical for materials prepared by

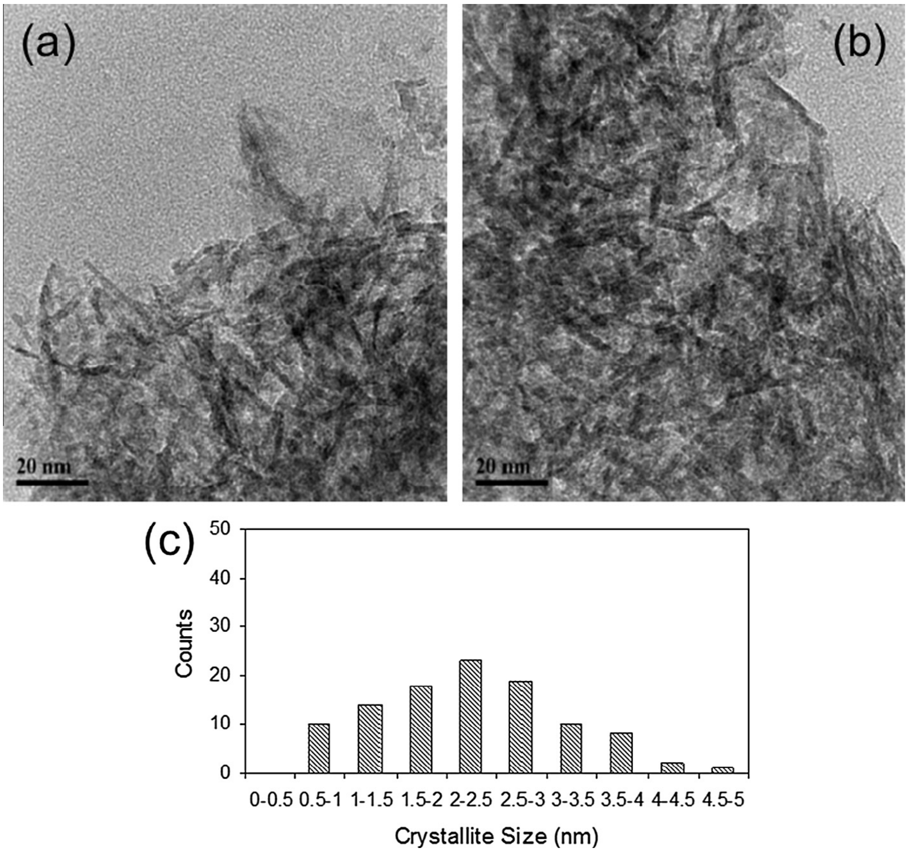


Fig. 2. (a) and (b) TEM images of 5 wt% Cu/Al_2O_3 (avg size ~2.6 nm); (c) crystallite size distribution of 5 wt% Cu/Al_2O_3 (avg size ~2.6 nm).

this method [30–32]. The Cu crystallites are visible as dark spots; the average crystallite size of the Cu nanoparticles was ~2.6 nm. In contrast, in the sample prepared by wet impregnation of copper onto Merck γ-Al_2O_3, the Cu (1 1 1) reflex could be clearly detected in the X-ray diffractogram (Fig. S1), and the crystallite size calculated from the Scherer equation was 7.0 nm.

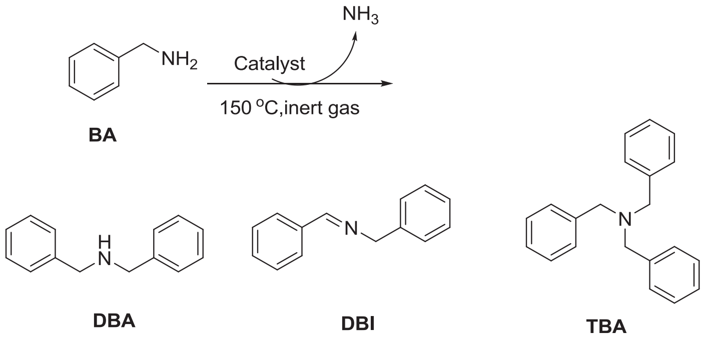
3.2. Catalytic performance

The catalysts were screened for their activities in the self coupling of benzylamine, and the conversions of benzyl amines after 24 h are summarized in Table 1. The selectivity to the secondary amine, dibenzylamine (**DBA**), was compared among the various catalysts (Table 1).

To start our investigations, the test reaction chosen was the self-coupling of benzyl amine. No products were formed in the absence of a catalyst (Table 1, entry 1). Similarly, both γ-Al_2O_3 samples, synthesized from aluminum tri-*sec*-butoxide and obtained commercially, have by themselves no activity for self coupling of benzylamine (Table 1, entries 2 and 3). A 5 wt% Cu/Al_2O_3 prepared from aluminum tri-*sec*-butoxide and H_2-activated before use gave 95% conversion after 24 h (Table 1, entry 8). The secondary amine, dibenzylamine (**DBA**) was the major product (96%) and the by-product accounting for the remaining 4% was identified as the imine, N-benzylidene-1-phenylmethanamine (**DBI**). The addition of a base promoter, Cs_2CO_3, had no positive effect on the reaction (Table 1, entry 10). Activation of the catalyst by pretreatment in a H_2 flow is essential; without this activation step, no products were detected (Table 1, entry 7). This indicates that copper metal and not copper oxide is the active species for the transformation. The H_2 treatment results in the formation of active metallic copper particles and removal of any adsorbed oxygen. In order to verify whether the hydrogen incorporated into **DBA** comes from hydrogen adsorbed at the metal surface during activation or indeed from the dehydrogenation of benzylamine, the reduced catalyst was flushed with N_2 at 300 °C for 1 h. This treatment was assumed to remove all physisorbed hydrogen from the catalyst. The conversion and selectivity were unaffected by this treatment (Table 1, entry 9), confirming that the hydrogen that is incorporated into the **DBA** originates from the dehydrogenation of benzylamine. The Cu/Al_2O_3 catalyst prepared by *in-situ* support formation is more active than that prepared by wet impregnation (Table 1, entry 15). After the standard reaction time, the conversion over this impregnated catalyst, 5% Cu/Al_2O_3-I, was only 60%, whereas it was 96% for the corresponding metal-entrapped 5% Cu/Al_2O_3. The lower activity of Cu/Al_2O_3-I is possibly due to the lower reactivity of the atoms at the surface of bigger Cu clusters (mean size 7.0 nm) as compared to that for 5% Ag/Al_2O_3 (mean size 2.9 nm).

The yield of **DBA** obtained over 5 wt% Cu/Al_2O_3 is much higher than that with 5% Ru/Al_2O_3, 5% Pd/Al_2O_3 and 2.4% Ag/Al_2O_3. After 24 h, >90% yield for **DBA** was obtained over Cu/Al_2O_3 but the yield was only 27% for 5% Pd/Al_2O_3 and 0.57% for 5% Ru/Al_2O_3, respectively. Over Ag-based catalysts, the conversion was 19% after

Table 1
Self-coupling of benzyl amine in the presence of different catalysts.



	Catalysts	Additives	Conv. (%)	DBA (%)	DBI (%)	TBA (%)
1	–	–	–	–	–	–
2	Al_2O_3[a]	–	–	–	–	–
3	Al_2O_3[b]	–	–	–	–	–
4	2.4% Ag/Al_2O_3	–	19	0	100	–
5	5% Pd/Al_2O_3[c]	–	100	27	73	–
6	5% Ru/Al_2O_3	–	19	3	97	–
7	5% Cu/Al_2O_3[d]		–	–	–	
8	5% Cu/Al_2O_3	–	95	96	4	–
9	5% Cu/Al_2O_3[e]		90	92	8	
10	5% Cu/Al_2O_3	Cs_2CO_3	84	76	24	–
11	5% Cu/AlOOH	–	10	0	100	–
12	5% Cu/MgO	–	10	0	100	–
13	5% Cu/SiO_2	–	19	0	100	–
14	5% Cu/ZrO_2		27	10	90	
15	5% Cu/Al_2O_3-I[f]	–	60	75	25	
16	5% Cu/Al_2O_3[g]	–	80	1	99	

Reaction conditions: **BA** 2 mmol, p-xylene 5 ml, catalyst 150 mg, Al_2O_3 200 mg, 24 h, He 1 atm.

[a] Commercial Al_2O_3 from Merck.

[b] Calcined from AlOOH, prepared by hydrolyzing aluminum tri-*sec*-butoxide.

[c] Conversion after 3 h at 100 °C.

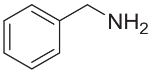
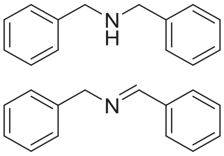
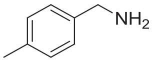
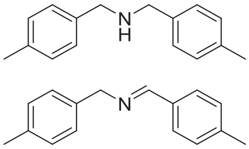
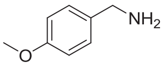
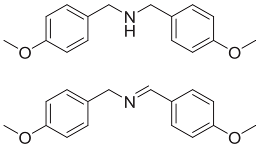
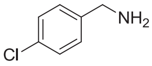
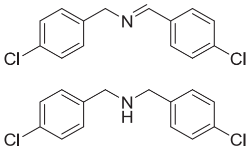
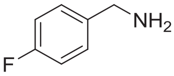
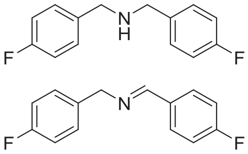
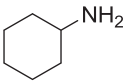
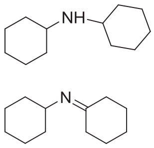
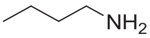
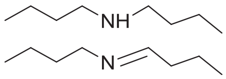
[d] Without H_2 pre-reduction.

[e] Treated in flowing N_2 (300 °C/1 h) after H_2 activation.

[f] Prepared by wet impregnation of commercial γ-Al_2O_3.

[g] Reaction conducted in system open to air.

Table 2
Self coupling of various amines.

	Amine	*t* (h)	Products	Conv. (%)	Sel. (%)	
					Amine	Imine
1		24		95[a]	96	4
2[a]		24		85[b]	83	17
2[a]		48		96[b]	95	5
3[c]		24		80	1	99
4		24		95	17	83
5		48		100	95	5
6		24		50	21	79
7		48		84	78	22
8		24		35	0	100
9		48		55	0	100
10		24		40	0	100
11		48		70	0	100
12		48		43	24	76
13		48		15	100	0

Reaction condition: amine 2 mmol, catalyst 5 wt% Cu/Al_2O_3 150 mg, 150 °C, 1 atm He in 22 ml autoclave.

[a] First use.

[b] Recycled.

[c] In 1 atm air.

24 h, but no **DBA** product was obtained. When the reaction was allowed to run for a longer time (30 h), a slightly higher conversion (21%) with 10% selectivity to the **DBA** was observed. The low conversion indicates a much lower activity of silver in the dehydrogenation of amines than of alcohols. Comparing the conversion on a molar basis, the intrinsic activity after 24 hour reaction decreased from 16, over 11 to 5 mol benzyl amine converted per mol of metal for the alumina-supported Cu, Ag and Ru catalysts after 24 h inside the autoclave reactor, respectively. For the Ag, Ru and Pd catalysts, the main product was the secondary imine **DBI** with the elimination of NH_3 and H_2. Surprisingly, the commercial 5% Pd catalyst was more active (28 mol/mol metal) than the supported Cu or Ru catalysts, and full conversion was obtained after 3 h at 100 °C. However, the selectivity toward **DBA** was only 27% as compared to >90% for the copper-based catalyst. The optimal catalyst system for the reaction was determined to be Cu/Al_2O_3 with a turnover numbers of 16.

The applicability of the heterogeneous Cu/Al_2O_3-catalyzed for the self-coupling of amines was examined using various combinations of substrates (Table 2). In all experiments, the amount of catalyst was adjusted so that the total metal was 5.9 mol%. p-Xylene was used as solvent, and reactions were run at 150 °C. Various derivatives of benzyl amine were evaluated for the reaction. All ring-substituted benzylamines coupled at a slower rate than benzyl amine, and gave the imine as the main product after 24 h (Table 2, entries 4, 6, 8 and 10). The return of the "borrowed hydrogen" that had been eliminated from the amine appears to be a very slow process, and substantial amounts of hydrogen can somehow be stored in the system. This hydrogen can be returned over a long time. When the reaction time was extended, we observed that the imine was slowly converted to the secondary amine when the substrates were aromatic amines bearing electron rich functional groups. In the closed reaction system, high yields of the saturated amine were obtained with 4-methylbenzylamine (95%) and 4-methoxylbenzylamine (66%) after 48 h (Table 2, entries 5 and 7). Even halogenated benzylamines can be used as electrophiles. 4-Chloro and 4-fluoro benzylamines give the unreduced secondary imine as the only product, with

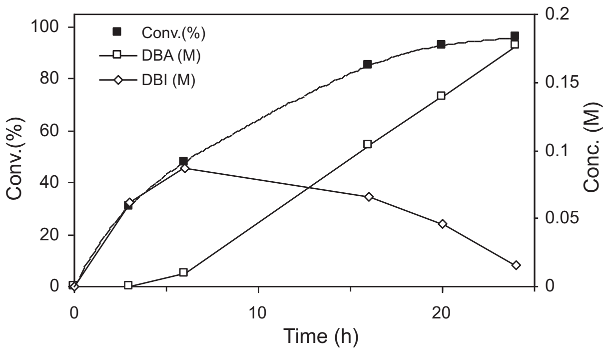
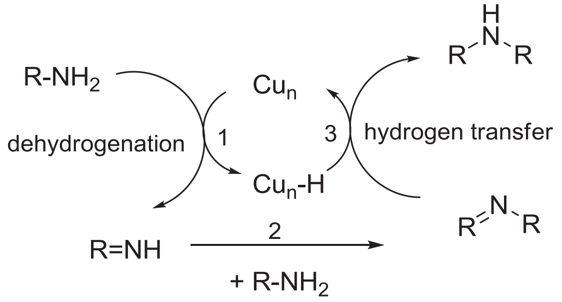


Fig. 3. Time-yield plots for self-coupling of benzylamine over 5 wt% Cu/Al_2O_3 (2.6 nm). Reaction conditions: amine 2 mmol, p-xylene 5 ml, catalyst 150 mg, conversion and selectivity from independent reactions (after 3, 6, 16, 20 and 24 h). (■) Conversion, (□) dibenzylamine, (◇) N-benzylidene-1-phenylmethanamine.



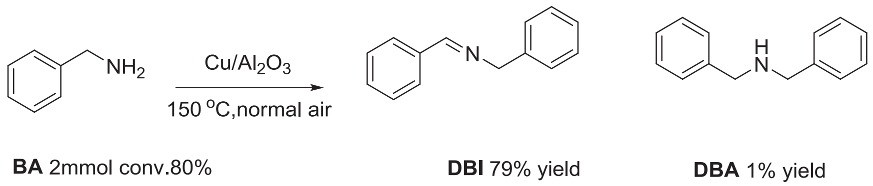
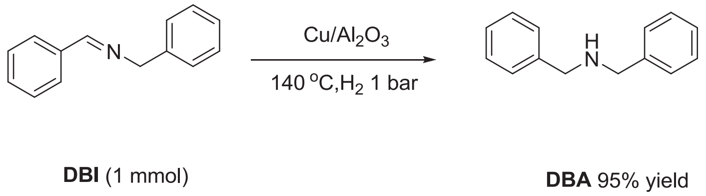
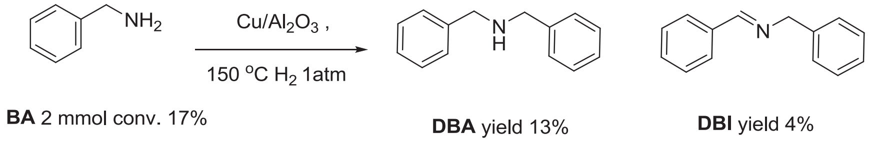
Scheme 2. Proposed reaction pathway of the Cu/Al_2O_3 catalyzed self coupling of amines.

the formal elimination of NH_3 and H_2. The catalyst system is not limited to aromatic amines. However, the activities for the coupling of linear and cyclic amines were substantially lower due to the instability of the intermediate R—C═NH (R: alkyl). N-Butyl amine reacts with itself to give N,N-dibutylamine in a poor yield of 15%, but with 100% selectivity after 48 h (Table 2, entry 13). Self coupling of cyclohexylamine gave dicyclohexylamine with a yield of 10%, together with 32% of the imine, and 67% of unconverted starting material. When a mixture of two different primary amines was used, GCMS of the reaction mixture showed all the expected products. In a test, equal amounts of benzyl amine $R—NH_2$ (1 mmol) and 4-methylbenzyl amine $R'—NH_2$ (1 mmol) were reacted under the standard conditions. After 24 h, a mixture of the expected products R_2NH, RR′NH, and $R_2'NH$ was obtained. The selectivity of the amine coupling can be increased if one amine component is unable to undergo oxidation such as anilines.

In order to test for leaching and to confirm that the reaction is indeed heterogeneously catalyzed, the reaction was allowed to run initially in the presence of the 5% Cu/Al_2O_3 catalyst (Fig. S3). After 3 h, when the conversion had reached about 30%, the reaction was stopped by cooling to open the reactor. The catalyst was recovered by centrifugation, and the clear supernatant was returned to the autoclave and subjected to further reaction. However, the conversion was unchanged after another 21 h and no further reaction was observed. In another experiment, the reaction mixture was withdrawn from the autoclave, heated again to boiling (bp of p-xylene is 138.4 °C) and the catalyst was then removed by hot filtration through a glass frit. The filtrate was returned to the autoclave, and again no more conversion was observed. These experiments confirm that the reaction is heterogeneously catalyzed, and the active phase did not leach from the catalyst under the reaction conditions.

The activity of 5% Cu/Al_2O_3 was tested for reuse. After the reaction was completed, the Cu/Al_2O_3 catalyst was recovered by filtration, first washed with large isopropanol, followed by acetone, recalcined and reactivated in H_2 at 300 °C before its use. There was some drop in the conversion (95% to 85%), which could be due to the sintering of copper crystallite on the support as copper is known to have a low Hüttig temperature of <300 °C. Electron micrographs of the used catalyst showed indeed an increase of the copper crystallite size from 2.6 nm to 4.1 nm (Fig. S4). However, comparable conversion (96%) as in the first run could be obtained if the reaction time was extended to 48 h. Surprisingly, after 24 h, the composition of the reaction mixture contained about 14% imine together with 70% saturated amine and 17% unconverted amine; after an additional 24 h period, the amount of saturated compound increased to over 91%, and that of the imine decreased to below 5%, with only 4% of starting material remaining. This indicates that the "borrowed" hydrogen has a very long life time. The experiment also shows that the loss of activity is not caused by a loss of catalyst during the recovery

Table 3
Reaction studies and conditions in the self coupling of benzyl amines.

	Reaction	Conditions
1	 	Normal air; 5 wt% Cu/Al_2O_3 (150 mg), 150 °C, 24 h
2	 	H_2 (1 bar) 5 wt% Cu/Al_2O_3 (150 mg), 140 °C, 24 h
3	 	H_2 (1 bar) 5 wt% Cu/Al_2O_3 (150 mg), 150 °C, 24 h

and regeneration process, but that changes to the catalytic sites influenced primarily the speed of hydrogenation of the imine, and did less affect the coupling reaction. Particularly remarkable is the capability of the catalyst to store very large amounts of hydrogen – there are only 5 mol% Cu in the system, but more than 14 equivalents of imine have been accumulated after 24 h, which are reacting with the "borrowed" hydrogen so that at the end of the reaction after 48 h, only 4.8 equivalents of imine were left.

3.3. Mechanistic studies

Fig. 3 shows the reaction profile of the reactants in the self coupling of benzylamine to produce **DBA** catalyzed by 5 wt% Cu/Al_2O_3. During the reaction, only two products, dibenzylamine **DBA** and N-benzylidene-1-phenylmethanamine **DBI**, were detected. The reaction profile shows the consecutive transformation of benzylamine, first to **DBI** and then to **DBA**. The concentration of **DBI** increased to a maximum at 6 h before decreasing with time as it transformed to **DBA**. The result in Fig. 3 showed that there are three-step consecutive reactions, i.e. dehydrogenation of **BA**, imine **DBI** formation, and imine **DBI** hydrogenation to **DBA**. The hydrogenation step 3 is faster than step 1, the imine formation, as the saturated secondary amine becomes the dominant species from 12 h onwards. This could suggest that $R{-}NH_2$ is involved in the rate-limiting step and **DBI** hydrogenation is not involved in the rate-limiting step. The results also rule out the hydrogenation of **DBI** by Cu—H species to regenerate Cu sites as the rate determining step.

Using gaseous hydrogen, N-benzylidene-1-phenylmethanamine **DBI** was readily reduced to dibenzylamine **DBA** with a yield of 95% (Table 3, entry 2). An inert atmosphere is essential to ensure that the reaction can proceed to the desired product **DBA** because under aerobic conditions, self coupling of benzyl amine gives exclusively **DBI** (Table 3, entry 1). Apparently, in the presence of oxygen, the "borrowed hydrogen" is immediately converted to water, and therefore no longer available for the subsequent hydrogenation step. Surprisingly, a H_2 atmosphere also inhibited the reaction, and the self coupling of benzylamine gave only 13% yield (Table 3, entry 3). In the presence of H_2, adsorption and dissociation will take place at the surface of the catalyst, leading to a high coverage of H atoms. This apparently inhibits the initial step of the reaction sequence, that is, the dissociation of the N—H bond of the amine. Since the reaction was performed under He, it is reasonable to assume that imine **DBI** was hydrogenated by the hydrogen species formed by the dehydrogenation of **BA**.

Based on these observations and the mechanism that has been proposed for ruthenium complexes [17] and Pd [24] catalysts, we propose that the reaction proceeds with the transitory formation of a Cu hydride species (Scheme 2). The initial step involves the removal of a hydride from the amine by the Cu catalyst leading to the formation of the imine compound. The imine readily reacts with a primary amine to form the corresponding secondary imine. The hydrogen apparently is stored in the support by some spillover effect. Here, γ-alumina or similar alumina phases seem to be more effective than other support materials. Finally, all the hydrides borrowed by the Cu metal from the primary amine are transferred back to the imine to afford the corresponding secondary amine.

4. Conclusions

In summary, we have demonstrated that Al_2O_3-supported copper catalysts act as an effective heterogeneous catalyst for the self coupling of amines, including aromatic and linear amines. The copper-based catalysts were generated by *in-situ* precipitation of a copper precursor together with an aluminum oxy-hydroxide support, followed by calcination at 600 °C. The reaction proceeds through the hydrogen-borrowing mechanism. The catalytic activity (TON) is found to be 16. The fundamental information gained from this study will enable the design of new catalysts and new process using amines as electrophiles for hydrogen-autotransfer catalysis for the environmentally benign production of chemicals.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.05.029.

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