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ARTICLE

Alumina-entrapped Ag Catalyzed Nitro Compounds Coupling with Alcohols Using Borrowing Hydrogen Methodology

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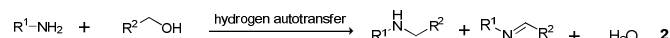
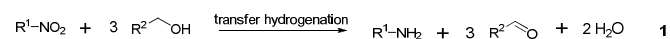
Supported silver catalysts were reported for the first time to be able to catalyze the coupling reaction between nitroarenes and alcohols via the borrowing hydrogen scheme. The recyclable, non-leaching catalyst is synthesized by the entrapped method, which allows entrapping silver nanoparticles in an alumina matrix. Alcohols, acting as the reducing agents for nitro-group, alkylated the resulting amines smoothly over these silver catalysts giving a yield of > 98% towards the N-substituted amines. In this process, multiple steps were realized in one-pot over a single catalyst with very high efficiency. It offers another clean and economic way to achieve amination of alcohols.

Introduction

Aromatic amines are important building blocks for the synthesis of pharmaceuticals, natural products, functional materials and agrochemical compounds [1]. N-substituted amines are usually prepared by the alkylation of amines with halides [2]. However, over alkylation and the generation of unwanted byproducts are commonly encountered problems with this method, which limit its application for the synthesis of secondary amines [3]. Several approaches have been developed to overcome these drawbacks, such as the hydroamination of olefins and alkynes [4] but this method is severely limited by the availability of the corresponding olefin and the electrophilic character of the nitrogen reagent. Recently, the catalytic alkylation of amines with alcohols [5] using the hydrogen autotransfer process [6], also known as borrowing hydrogen [7] or self-supplying system for active hydrogen [8] has been proposed as an environmental benign procedure to produce N-substituted amines. Alcohols are readily available, relatively cheap and nontoxic, and theoretically, water is the only byproduct. However, alcohols are poor electrophiles and therefore not suitable as direct alkylating agents for amines. But alcohols can be readily activated by oxidation to aldehydes or ketones, which are then used for the alkylation. In a typical alkylation reaction using alcohols as the alkylating agents via the borrowing hydrogen methodology, the poorly electrophilic alcohol is first converted into an aldehyde with the liberation of one molecule of H₂, probably in the form of a metal hydride. The aldehyde reacts with the amine to form an imine under elimination of one molecule of water. The imine is then reduced by the metal hydride to obtain the final product. This interesting transformation has been studied extensively since the first reports by Grigg [9] and Watanabe [10], and recently, various heterogeneous catalysts based on transition metals such as Ag [11], Pd [12], Ru [13] and Au [14] have been described for amination of alcohols using amines as the nitrogen source. Despite the importance of the N-substituted amines, to date, the selective synthesis of N-substituted amines through borrowing hydrogen methods was restricted to the reaction of amines with alcohols. It is still a challenge to extend the methodology to a wider range of substrates. Nitroarenes are another class of cheap and readily available organic compounds and it is much

less used as the nitrogen source compared with amines. Furthermore, the use of nitroarenes as the nitrogen source in the one-pot tandem amination is even more challenging due to the difficulty of selective reduction of nitro groups [15]. Several catalytic systems for the one-pot reductive aminations of aldehydes with nitroarenes have been recently developed, including the following: pyridinium dichromate/Wilkinson's catalyst in sol-gel matrices [16], H₂/Pd/C [17, 18], palladium nanoparticles [19], H₂/Au/Fe₂O₃ [20], and Au-Pd/Al₂O₃ [21]. A tandem process for the preparation of imines from nitroarenes with alcohols can be achieved by using an Ir-Pd bimetallic complex as the catalyst [22]. Both nitroarenes and alcohols are cheap and readily available organic compounds, and developing reactions that use nitroarenes and alcohols as starting materials is highly attractive, especially when a single catalyst system could be employed in this multistep reaction.

In this valuable one pot multistep transformation (Scheme 1), the alcohol may conceivably serve two possible functions: as the hydrogen source for reduction of the nitro-group and as the alkylating reagent based on the catalytic hydrogen transfer. Although excess alcohol (four equivalents of alcohols) is required to ensure completion of the reaction, the operational simplicity of this transformation may have practical advantages for the concise synthesis of N-substituted amines.



Scheme 1. Bifunctions of alcohols in the reductive N-alkylation of nitroarenes with alcohols (1) hydrogen source for the reduction of nitro group (2) hydrogen source for the reduction of secondary imine

Homogeneous Ru [23, 24] catalysts have been reported to be active in the reductive amination of alcohols with nitroarenes. Deng et al. reported that N-substituted amines can be obtained from nitroarenes and nitriles using a homogeneous ruthenium complex [24]. Complete conversion was obtained after 12 h at 130 °C. However, homogeneous metal catalysis suffers from difficulties of recycle and reuse, which results in loss of expensive metals and is a serious economical drawback. From a

sustainability point of view, a more efficient reaction with a ligand-free heterogeneous catalyst is highly desired. However, to date, only Au and Ru based catalysts such as Au/TiO₂ [25], Au/Fe₃O₄ [26] and Ru(OH)₃/Fe₃O₄ [27] have been reported for the one-pot synthesis of N-alkylated anilines from nitroarenes and alcohols. Cao et al. described the formation of secondary amines via N-alkylation of nitroarenes. The reaction was almost quantitative after 14 hours at 120 °C using alcohols over a nanosized Au/TiO₂. Yus's group from Spain screened various impregnated metallic salts on magnetite, including cobalt, nickel, copper, ruthenium, and palladium salts, as well as a bimetallic palladium–copper derivative and they found only impregnated ruthenium catalyst was active for the selective N-monoalkylation of aromatic amines and a yield of 5 – 99 % was obtained for different substituted nitroarenes at 130 °C for 3 days with 130 mol% KOH additives.

Our group have shown that entrapped Ag clusters act as efficient heterogeneous catalyst for the clean and atom-efficient mono-N-alkylation of a range of amines with alcohols under hydrogen-borrowing conditions [11]. In view of the prominent efficiency of the silver system for the amination of amines with alcohols, we envisioned that the Ag-mediated hydrogen-borrowing strategy could also afford a green and efficient protocol for the direct amination of nitroarenes with alcohols under mild conditions. We observed that the Ag/Al₂O₃ system does indeed catalyze the selective formation of secondary amines from nitroarenes and alcohols. Notably, the reaction proceeds effectively without any external hydrogen source. To the best of our knowledge, this study forms the first report of a one-pot selective preparation of amines from nitroarenes and alcohols by the heterogeneous silver-mediated catalytic hydrogen transfer procedure.

Results & Discussion

The catalyst was synthesized as previously described [11]. The 2.4 wt% Ag/Al₂O₃ has a surface area of 281 m² g⁻¹, with the hysteresis loops typical of mesoporous structure. As previously described, the 2.4 wt% Ag/ Al₂O₃ showed the fibrous nature of the support which is typical of the materials prepared by this method [28] and the average silver crystallite size of Ag for 2.4 wt% Ag/ Al₂O₃ was measured to be 1.7 nm from the TEM image measurement (Fig S1) and no obvious Ag metal aggregation was observed after the reaction.

For sample with 2.4 wt% Ag, only the broad peaks of γ -Al₂O₃ support were shown on the powder X-ray diffractograms and the absence of reflexes due to Ag suggests that the metal is well dispersed on the support and/or that the crystalline size of Ag nanoparticles is below the detection limit of X-ray diffractometry, typically less than 4 nm and the crystallite size of 2.4 wt% Ag from the transmission electron micrographs of were ~ 1.7 nm. In comparison with the alumina-entrapped Ag catalyst, the sample prepared by wet impregnation had higher \Ag particles and the Ag crystallite size was calculated to be 5.4 nm from the Scherrer equation for 2.4 wt% Ag/Al₂O₃ prepared from wet impregnation method (Fig S2).

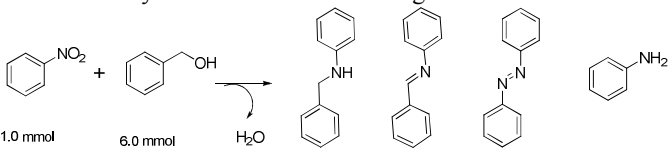
To study electronic structures of Ag nanoparticles on Al₂O₃ surface (Fig S3), XPS was used. For the Ag nanoparticles with an average diameter of 1.7 nm for 2.4 wt% Ag/Al₂O₃ catalyst, a core level shift of +0.3 eV was observed compared to the 3d levels of Ag bulk crystals (Fig S3). The positive core level shifts have been reported for metal nanoparticles on less

conductive substrates [29]. For smaller clusters on less conductive substrates, the positive hole, can be less efficiently screened, causing a positive core level shift and the initial state effect can also contribute to the positive chemical shifts, since changes of valence band positions or depletion of valence band electrons with decreasing particle size can affect the core level shifts. Increased lattice strain with decreasing particle size can also contribute to the positive core level shifts by initial state effect and typically, a chemical shift of 0.5-2.0 eV can be seen for small nanoparticles compared to the core levels of the respective bulk crystals. This could also suggest that the Ag nanoparticles on Al₂O₃ show more irregular shapes compared to the bulk Ag, leaving higher densities of undercoordinated atoms on the surface of the Ag particles support compared to those from bulk Ag and these unsaturated atoms play an important role in the catalysis reactions.

The optimization study was initiated with the direct amination of nitrobenzene. The stoichiometry of the reaction requires four equivalents of benzyl alcohol for every molecule of nitrobenzene. However, in order to achieve a higher conversion of the nitrobenzene, the alcohol was used in excess, at a ratio of 6:1. All reactions were conducted in the presence of the selected catalysts for 19 h at 140 °C under an atmosphere of flowing nitrogen. The results are summarized in Table 1. The corresponding secondary amine, N-phenylbenzylamine (3), was the main C-N cross coupling product. Benzyl alcohol and nitrobenzene did not form any products in the absence of the catalyst (Table 1, entry 1). Similarly, the γ -Al₂O₃ support or Cs₂CO₃ alone had no activity for the N-alkylation of aniline with benzyl alcohol (Table 1, entries 2-3). The 2.4 wt. % Ag/ Al₂O₃ catalyst prepared from aluminium tri-sec-butoxide and activated under H₂ before use gave 36 % conversion after 19 h (Table 1, entry 4). The secondary amine, N-phenylbenzylamine 3, and the imine, N-benzylideneaniline 4, were formed in almost equal amounts (41:59). As had been already observed in the case of the N-alkylation of amines with alcohols, the addition of a base promoter, Cs₂CO₃, led to a tremendous increase in the activity so that > 99 % conversion was obtained (Table 1, entry 8). Equally striking is the very high selectivity, 98 %, to N-phenylbenzylamine 3. The only other product formed was the imine 4. As the addition of Cs₂CO₃ increased the activity significantly, other basic promoters were investigated (Table 1, entries 5,6,8). The results show that Cs₂CO₃ is the most effective promoter among the three alkali metal carbonates tested, i.e. Na₂CO₃, K₂CO₃ and Cs₂CO₃. The activity of 2.4 % Ag/Al₂O₃ was tried for reuse to evaluate its stability. After 98% yield of the target compound 3 were obtained after 20 h, fresh substrate (1 mmol nitrobenzene and 6 mmol benzyl alcohols) was added, and after 22 h, full conversion with 95% selectivity to the target compound was again obtained. Full conversion after 24 h can still be obtained up to the third run (Fig. S4). Following the batch reaction, the catalyst was recovered by filtration, washed with isopropanol, followed by acetone, and reactivated in H₂ at 300 °C. The rate of reaction was very similar to that of the fresh catalyst, and N-phenylbenzylamine was formed with 97 – 98 % selectivity at

99 % conversion (entry 9-10). The catalytic activity of 2.4 wt.% Ag/Al₂O₃ together with a base promoter is higher than that of 5 % Ru/Al₂O₃ or 5 % Pd/Al₂O₃. Under the conditions described in Table S1, Cu, Ru or Pd nanoparticles supported on Al₂O₃ were not effective (Table S1, entry 12-14), illustrating that silver is far superior to other noble metals for the direct reductive mono-N-alkylation of 1 with 2.

Table 1 N-alkylation of nitroarenes using alcohols



1	2	3	4	5	6		
Catalysts	Add.	Cond.	Conv.	Sel.(3)	Sel.(4)	Sel.(5)	Sel.(6)
1	--	N ₂	--	--	--	--	--
2	Cs ₂ CO ₃	N ₂	--	--	--	--	--
3	Al ₂ O ₃	Cs ₂ CO ₃	N ₂	--	--	--	--
4	Ag/ Al ₂ O ₃	--	N ₂	36	41	59	0
5	Ag/ Al ₂ O ₃	Na ₂ CO ₃	N ₂	100	51	49	0
6	Ag/ Al ₂ O ₃	K ₂ CO ₃	N ₂	100	91	2	7
7	Ag/ Al ₂ O ₃	Cs ₂ CO ₃	Open air	33	2	13	80
8	Ag/ Al ₂ O ₃	Cs ₂ CO ₃	N ₂	100	98	2	0
9	Ag/ Al ₂ O ₃ ^a	Cs ₂ CO ₃	N ₂	100	97	3	0
10	Ag/ Al ₂ O ₃ ^b	Cs ₂ CO ₃	N ₂	100	98	2	0
11	Au/ Al ₂ O ₃ ^c	Cs ₂ CO ₃	N ₂	100	21	48	26
12	Cu/ Al ₂ O ₃	Cs ₂ CO ₃	N ₂	39	3	41	56
13	Pd/ Al ₂ O ₃	Cs ₂ CO ₃	N ₂	52	0	51	0
14	Ru/ Al ₂ O ₃	Cs ₂ CO ₃	N ₂	20	0	100	0

Reaction condition: nitrobenzene 1 mmol, benzyl alcohol 6 mmol, basic additives 100mg, xylene 5 ml, Cat 2.2 mol%
a: 2nd run b: 3rd run c: Au 1.1 mol%

Subsequently, the reaction conditions were optimized with the Ag/Al₂O₃ catalyst through variation of the benzyl alcohol 2/nitrobenzene 1 ratio (Table S1). Studies on the effect of the molar ratio of benzyl alcohol to nitrobenzene revealed that the reaction of nitrobenzene with six equivalents of benzyl alcohol gave the best results. The use of three equivalents of benzyl alcohol leads to incomplete conversion of nitrobenzene. The azobenzene 5, which is a nitrobenzene hydrogenation intermediate, was the dominant product, and only a trace amount of the desired N-phenylbenzylamine 3 could be obtained. Upon increasing the benzyl alcohol/nitrobenzene ratio from three to six, the reaction proceeded to completion along with a significant increase in the yield of the product N-phenylbenzylamine 3. Further increase of benzyl alcohol did not have a beneficial effect on the yield. This result suggests that the composition of the reaction medium was critical for the desired reaction pathway.

To optimize the N-alkylation of nitrobenzene by benzyl alcohol, the effect of silver loading on the Ag/Al₂O₃ catalyst was studied. The initial reaction rate (determined from the conversion after 1 h) increased steeply up to 2.4 wt. % Ag, before decreasing slightly (Fig. 1a). At higher Ag-loading, the average size of the metal crystallites increases, so that fewer atoms are in the surface where they are catalytically active. Smaller crystallites have relatively more atoms in the surface (higher dispersion). The TOF based on total atoms calculated from the initial rate, decreased from 36 h⁻¹ to 0.9 h⁻¹ as the Ag loading increased from 0.59 to 13 wt. %. The good activity of the catalysts with metal loading from 0.59 to 6.2 wt. % Ag is also seen in their turnover numbers, 16 – 183.

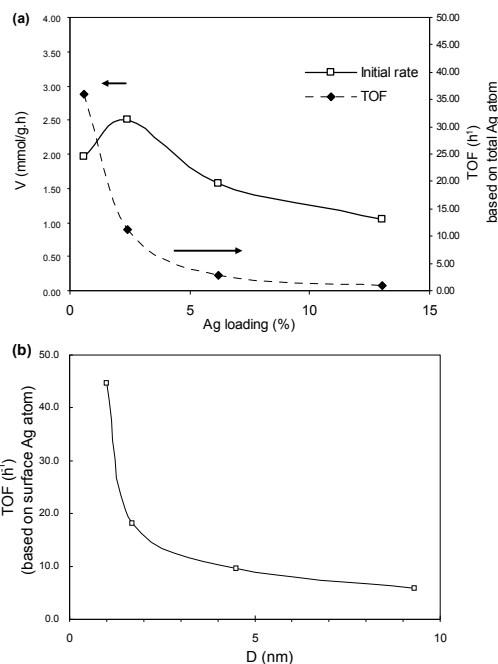


Figure 1. (a) Silver loading of Ag/Al₂O₃ catalysts on N-alkylation of nitrobenzene by benzyl alcohol. TOF values for the conversion of aniline given as the ratio of moles of aniline per mole Ag per hour (measured at t = 1 h) versus the loading of silver (b) TOF based on the number of surface Ag atoms for conversion of nitrobenzene to secondary amine/imine at 140 °C as a function of average particle size of Ag in Ag/Al₂O₃ catalysts. Reaction conditions as described in Table 1

To investigate the relationship between the Ag-crystallite size and the catalytic activities, catalysts with Ag-content of 0.5 wt%, 2.4 wt% and 6.2 wt% were prepared and tested for their activities. By using the initial reaction rate in Fig 1a and the Ag crystallite size measured from the TEM images, the turnover frequency (TOF) based on surface Ag site was estimated and plotted versus Ag particle size (Fig 1b). The Ag cluster with the smallest particle size gave the highest activity. Taking into account the fact that the fraction of Ag atoms at corner and edge sites dramatically increased with a decrease in the Ag size, especially below a few nm, the dramatic increase in TOF below 2 nm suggests that the coordinately unsaturated Ag sites play an important role in the present system.

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 a 2.4 % Ag/Al₂O₃ catalyst (Fig. S5). After 2 h, the catalyst was removed from the reaction mixture by centrifugation. The clear supernatant was again brought to reaction conditions. Over a period of next 17 h, the conversion remained unchanged and no further reaction was observed. These experiments confirm that the active phase did not leach from the catalyst under the reaction conditions.

Other substrates

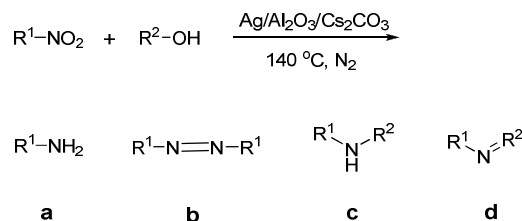
With suitable reaction conditions established, the applicability of the heterogeneous Ag/Al₂O₃ -catalyzed N-alkylation was examined using various combinations of substrates (Table 2).

	Alcohol	Nitroarene	T (h)	Conv (%)	Sel. (a)	Sel. (b)	Sel. (c)	Sel. (d)
1			19	100	0	0	98	2
2			24	100	0	0	42	58
3			36	100	24	0	76	0
4			24	100	0	0	85	15
5			24	100	0	0	25	75
6			36	100	0	0	76	24
7			36	100	11	0	0	89
8			15	100	0	0	99	1
9			15	100	0	0	99	1
10			19	100	0	0	98	2
11			19	100	0	0	97	3
12			19	100	53	47	0	0
13			19	100	0	29	43	28
14			19	67	68	32	0	0
15			24	11	47	53	0	0
16			24	19	40	60	0	0

As revealed in Table 2, various structural diverse nitroarenes with electron withdrawing as well as donating substituents on the aromatic ring could be mono-alkylated with benzyl alcohol to give the corresponding secondary amines with yields of 42 - 99% (Table 2, entry 1- 10). Compared to the direct coupling of substituted anilines and benzyl alcohol over $\text{Ag}/\text{Al}_2\text{O}_3$, the presence of substituents at the nitroarenes affected the reaction rate significantly. *p*-Chloronitrobenzene requires a much longer reaction time for complete reaction than *p*-methyl nitrobenzene (Table 2, entry 1 and 2). The reaction tolerates the presence of halogens (Table 2, entry 2,3,5-7). A much longer time is required for completion when the substituent was changed from fluoride to chloride, which could be due to the steric effect (entry 3 and 5). A substituent at the ortho position has a great impact on the reaction; the lower reaction rate of *o*-chloronitrobenzene relative to *p*-chloronitrobenzene (entry 2 and 3) and *o*-methylnitrobenzene to *p*-methylnitrobenzene (entry 1 and 4) indicated a steric effect. Furthermore, the reaction also proceeds successfully with other primary alcohols (entry 10-11). Linear alcohols were found to be inactive for the coupling reaction and the reaction stopped at the transfer hydrogenation of nitrobenzene (entry 15-16). Secondary alcohols were good hydrogen sources for the transfer hydrogenation of nitrobenzene, but generally inactive for the

subsequent coupling reactions (entry 12 and 14), possibly due to the steric effect.

Table 2 Results of the reductive alkylation of nitroarenes with alcohols



Reaction conditions: nitroarene 1 mmol, alcohol 6 mmol, Cs_2CO_3 100mg, xylene 5 ml, Cat 2.2 mol%

Mechanistic studies

Here we are trying to explore the reaction mechanism of the N-alkylation of nitrobenzenes with alcohols. The reaction of nitrobenzene and benzyl alcohol was studied and the time-yield plot for the N-alkylation in the presence of the catalyst is shown in Fig 2. The catalyst used was 2.4 wt.% $\text{Ag}/\text{Al}_2\text{O}_3$. Conversion and selectivity are based on nitrobenzene and have been determined by GC-FID. Four major N-containing compounds, i.e. aniline 6, azobenzene 5, N-phenylbenzylamine 3 and N-benzylideneaniline 4) were detected in the GC spectrum. Benzyl alcohol, which was present in six fold excess, also gives appreciable amounts of dehydrogenation byproducts including benzaldehyde and benzyl benzoate. As illustrated in Fig 2, azobenzene 5 was the dominant product for the first few hours, and aniline 6 was present in small amounts only, due to the fast condensation reaction with aldehyde to form N-benzylideneaniline 4. The concentration of N-benzylideneaniline 4 reaches a maximum at 3 h, then decreases with the time. The reaction profile shows the consecutive transformation of N-benzylideneaniline 4 to N-phenylbenzylamine 3 (Fig. 2). We have shown that the N-alkylation of aniline using alcohols proceeded via a borrowing hydrogen methodology.

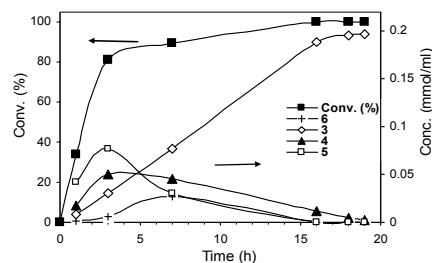
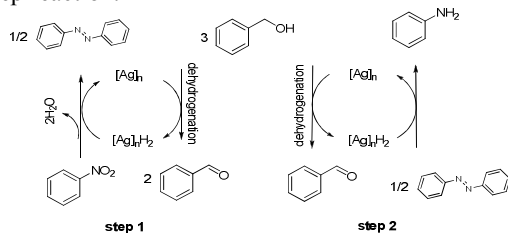


Figure 2. Time-yield plots for the N-alkylation of nitroarenes with benzyl alcohol in the presence of $\text{Ag}/\text{Al}_2\text{O}_3$. Reaction conditions: nitrobenzene 1 mmol, benzyl alcohol 6 mmol, *p*-xylene 5 ml, catalyst $\text{Ag}/\text{Al}_2\text{O}_3$ 100 mg, (■) conversion (◇) N-phenylbenzylamine 3 (▲) N-benzylideneaniline 4 (□) Azobenzene 5 (+) Aniline 6

The transfer hydrogenation of nitrobenzene to aniline could proceed via the azobenzene as the intermediate (Scheme 2). To find out the active species catalyzing the transfer hydrogenation of nitrobenzene to aniline, different alcohols including a linear secondary alcohol (2-butanol) and an aromatic alcohol (benzyl alcohol) were used as hydrogen donor (Table 3). A solid base

alone such as Cs₂CO₃ did not catalyze the transfer hydrogenation of nitrobenzene to aniline either using aromatic alcohol or secondary linear alcohols (Table 3, entry 1 and 2) even after 19 h. With a 2.4 wt% Ag/Al₂O₃ catalyst, up to 80% conversion of nitrobenzene 1 was obtained after 15 h in the closed system (autoclave) with 61 % selectivity to aniline 6 and the rest to azobenzene 5 (Table 3, entry 3). When the reaction was extended to 24 h, full conversion of nitrobenzene 1 was obtained and the selectivity to aniline 6 was 85%, the balance again being azobenzene 5 (Table 3, entry 4). This corresponds to a yield of 85%, which is slightly lower than that obtained during the reductive N-alkylation of nitrobenzene 1 with benzyl alcohol 2. This slightly decrease could be attributed to the lack of driving force as aniline produced was continuously consumed for the next coupling reaction with aldehyde in the multistep reaction.

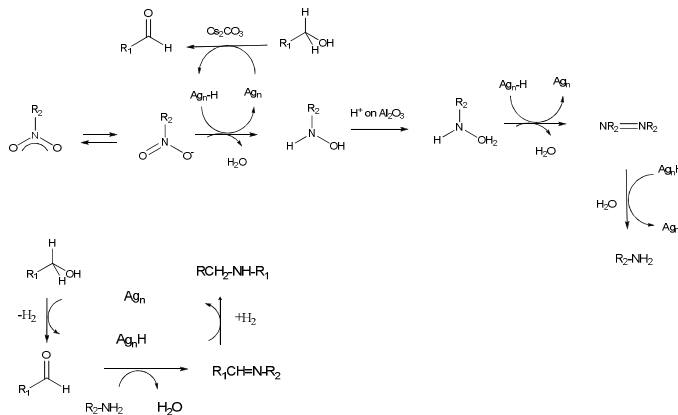


Scheme 2. Pathway of transfer hydrogenation of nitrobenzene to anilines by benzyl alcohol (1) transfer hydrogenation of nitroarenes to azobenzenes (2) transfer hydrogenation of azobenzenes to anilines

Table 3 Reaction studies and conditions.

Reaction	Conditions
1 NO METAL CATALYST Cs ₂ CO ₃ , 100 °C benzyl alcohol, 5 ml	N ₂ (1 bar), Cs ₂ CO ₃ (100 mg), 100 °C, 19 h no reaction
2 NO METAL CATALYST Cs ₂ CO ₃ , 100 °C benzyl alcohol, xylene 5 ml	N ₂ (1 bar) Cs ₂ CO ₃ (100 mg) 100 °C, 19 h no reaction
3 Ag/Al ₂ O ₃ , Cs ₂ CO ₃ benzyl alcohol, 5 ml, 15 h	N ₂ (1 bar) Ag/Al ₂ O ₃ (100 mg) Cs ₂ CO ₃ (100 mg) 100 °C, 15 h yield 48 %
4 Ag/Al ₂ O ₃ , Cs ₂ CO ₃ benzyl alcohol, 5 ml, 24 h	N ₂ (1 bar) Ag/Al ₂ O ₃ (100 mg) Cs ₂ CO ₃ (100 mg) 100 °C, 24 h yield 85 %

We have previously demonstrated that the N-alkylation of amines with alcohols proceeds via the borrowing hydrogen mechanism over silver catalysts [11]. Thus, a tentative reaction pathway to rationalize the transformation is illustrated in Scheme 3 starting from the nitroarenes and alcohols. First, the alcohol is oxidized into aldehyde catalyzed by the silver cluster promoted by base. Simultaneously, the hydride is transferred to the silver cluster to give a silver-hydride complex. This silver-hydride complex reduces the nitro group to first to azobenzene, and further to amine. In the next step, the amine reacts with the aldehyde to give the imine intermediate, which is reduced to the final product using the borrowed hydrogen. The reaction is multistep, catalyzed by the same catalyst in a one pot reaction.



Scheme 3. A tentative pathway for the direct alkylation of nitroarenes.

Experimental and Catalytic Testing

Synthesis of Ag/Al₂O₃ catalysts The alumina-supported Ag catalysts discussed were prepared with Ag loadings from 0.29 to 13 wt. % using the entrapped method. In a typical synthesis for a 2.4 wt. % Ag/Al₂O₃ sample, AgNO₃ (63 mg/0.37 mmol) and aluminium tri-sec-butoxide (8.32 ml/32.4 mmol) were dissolved in 2-butanol (1.98 ml). The resulting gel was stirred at 100 °C for 3 h to give a yellow suspension. At this point, 4.5 ml of deionized water were slowly added and the clear gel hydrolyzed instantly. Stirring was continued for another hour at 100 °C, before the suspension was allowed to cool to room temperature. The solid catalyst was filtered off, and the filter cake thoroughly 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 H₂ at 300 °C for 30 min. The same procedure was followed for preparing Cu/Al₂O₃ catalysts except that copper acetate was used. The metal content was determined by ICP-AES.

Characterization of Catalysts The surface area and pore volume were determined by nitrogen adsorption (micromeritics Tristar 2000). The sample was degassed under N₂ at 300 °C for 4 h prior to the measurement. X-ray diffraction (XRD) was measured with Cu-Kα X-ray radiation at λ=1.54056 Å with diffractograms recorded for 2θ between 30° and 90°.

X-ray photoelectron spectra (XPS) were acquired with a VG-Scientific ESCALAB Mark 2 spectrometer equipped with a hemispherical electron analyzer and an Mg Ka (1253.6 eV) X-ray source with power of 300 w (15 kV × 20mA). The binding energy calibration was performed using the C1 s peak at 284.6 eV as the reference energy.

Procedure for N-alkylation of nitroarenes using alcohols

The catalytic N-alkylation of nitroarenes using alcohols was carried out under N₂ at 140 °C in a 25 ml round bottom flask equipped with a condenser. Typically, 1.0 mmol nitrobenzene and 6 mmol of benzyl alcohol were dissolved in 5 ml p-xylene; 0.100 g catalyst and 0.1 g base promoter were added. Aliquots were removed at regular time intervals and analyzed by gas chromatography. The products were identified by GC-MS.

Conclusions

In conclusion, we have reported here the noteworthy features of an Ag/Al₂O₃ catalyst for the direct reductive mono N-alkylation of a range of aromatic nitro compounds with alcohols via a hydrogen-borrowing strategy. This process has significant

advantages when compared with other N-alkylation methods, such as (1) cheap and readily available reactants (nitroarenes and alcohols) (2) high catalytic activity and selectivity (3) no external molecular hydrogen or other stoichiometric reducing agents are necessary in our catalytic system and (4) the multi step reaction was one pot catalyzed by a single catalyst system. We believe that the reaction chemistry described here may enable the development of new sustainable processes for clean and efficient synthesis of secondary amines or anilines from nitroarenes with alcohols.

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Notes and references

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Notes

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