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Facile and efficient reductive *N*-alkylation of nitrobenzenes with alcohols catalyzed by Cu–Cr/γ-Al_2O_3

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Abstract A facile and efficient method for reductive *N*-alkylation of nitrobenzenes with alcohols catalyzed by the bimetallic catalyst $Cu_{30}Cr_5$/γ-Al_2O_3, in a fixed-bed reactor, was successfully established. X-ray diffraction, temperature-programmed reduction, and X-ray photoelectron spectroscopy were used to characterize the catalyst. Introduction of Cr to Cu_{30}/γ-Al_2O_3 was found to substantially enhance the dispersion of Cu^0 particles, which are believed to be the active sites for the reductive *N*-alkylation. The reaction conditions were optimized and a series of alcohols and nitrobenzenes were converted into *N*-alkylated anilines in more than 90 % yield by use of this catalyst.

Keywords Nitrobenzene · Alcohol · Reductive *N*-alkylation · Cu–Cr/γ-Al_2O_3

Introduction

N-Alkylamines are important compounds in the chemical industry and are extensively used for production of pharmaceuticals, agrochemicals, and fine chemicals [1, 2]. *N*-Benzylaniline, one of the most important *N*-alkylated anilines, is used as a building block for synthesis of dyes and surfactants [3], typically by alkylation of amines with alkyl halides [4–6] or reductive amination of aldehydes or ketones [7–9]. However, these processes are problematic, because of the toxic

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nature of alkyl halides, the generation of inorganic salts and harmful by-products, and the use of expensive carbonyl compounds. Use of alcohols as alkylating agents in green and economical processes has attracted much attention. Recently, *N*-alkylation of amines with alcohols, in which water is produced as the sole byproduct, has been demonstrated to be an alternative and environmentally friendly route for synthesis of *N*-alkylated amines by use of borrowing-hydrogen (or hydrogen-autotransfer) methodology. Several metal catalysts, for example iridium [10–13], ruthenium [14–18], palladium [19, 20], gold [21], and silver [22–24] have been reported to enable effective *N*-alkylation.

Because nitrobenzenes and alcohols are inexpensive and readily available, direct reductive *N*-alkylation of nitrobenzenes with alcohols would be a more convenient method for preparation of *N*-alkylated anilines. There are reports of direct synthesis of *N*-alkylated anilines in the presence of heterogeneous catalysts. In these systems, hydrogenation of nitroaromatics, dehydrogenation of alcohols to carbonyl compounds, and reductive *N*-alkylation of arylamines with carbonyl compounds can proceed in one reactor. Peng et al. [25] have reported the one-pot synthesis of *N*-alkylated anilines from nitroarenes and alcohols by use of an Fe_2O_3-supported nano-gold catalytic system. Schimizu et al. [26] investigated direct synthesis of *N*-substituted anilines from nitroaromatics and alcohols by use of alumina-supported silver catalysts. Another report by Tang et al. [27] described direct one-pot reductive *N*-alkylation of nitroarenes with alcohols by use of supported gold catalysts. More recently, Lee et al. [28] investigated the synthesis of alicyclic amines and subsequent *N*-alkylation with alcohols using Ru/C-$NaNO_2$. In our previous work [29–32] good performance was observed for copper-based catalysts in the amination of amines and alcohols. In this context, we report a method for the preparation of *N*-alkylated anilines from nitrobenzenes and alcohols catalyzed by Cu–Cr/γ-Al_2O_3 in a fixed-bed reactor. The effect of doping of Cu/γ-Al_2O_3 with Cr was studied by X-ray diffraction (XRD), H_2-temperature programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS). The activity and stability of $Cu_{30}Cr_5/\gamma$-Al_2O_3 in the reductive *N*-alkylation of nitrobenzene with benzyl alcohol were studied.

Experimental

Materials and catalysts

Nitrobenzene and benzyl alcohol were obtained from Tianjin Guangfu Fine-chemical institute, Tianjin, China. Pseudo boehmite was provided by Jiangyan Chemical Auxiliary Factory, Jiangyan, China. Commercially available solvents and reagents were used without further purification.

The γ-Al_2O_3-supported bimetallic catalysts were prepared by the coprecipitation-kneading method. For example, to prepare $Cu_{30}Cr_5/\gamma$-Al_2O_3 a mixture of 45.6 g $Cu(NO_3)_2\cdot 3H_2O$ and 15.4 g $Cr(NO_3)_3\cdot 9H_2O$ in 200 ml H_2O, and a solution of 28.3 g sodium carbonate in 200 ml H_2O were added dropwise, at ambient temperature with mechanical stirring, to a beaker containing 200 ml H_2O over 1 h then aged for another 1 h. During the process, the pH of the system was maintained at approximately 8. The precipitate was isolated by filtration, washed with distilled water, dried for 6 h at 110 °C, then kneaded with a mixture of 39 g pseudo-boehmite and 60 ml distilled water. This mixture was then molded into bars by use of an extruder. After drying in air for 6 h at 110 °C, the bars were calcined for 4 h at 500 °C then reduced at 240 °C in a hydrogen stream (1 MPa) for 4 h before later use.

Catalyst characterization

XRD patterns of the samples, in the range 5–95°, were recorded with a Rigaka D/max 2500 X-ray diffractometer with Cu-K_{α}(40 kV, 100 mA) radiation. Temperature-programmed reduction with H_2 was measured by use of a Micromeritics 2910 apparatus equipped with a thermal conductivity detector (TCD); calcined samples were heated from ambient temperature to 900 °C at 10 °/min in a mixture of 5 % H_2 in N_2. XPS measurements were recorded with a PHI 1600 spectrometer with an Mg-K_{α} X-ray excitation source.

Catalytic reaction

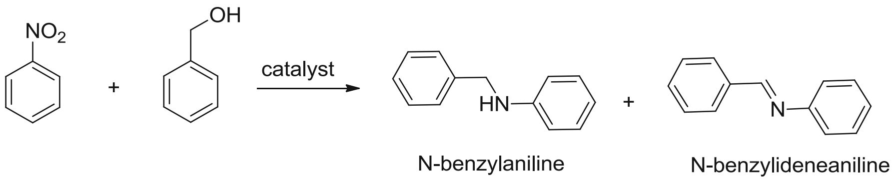
The reaction was conducted in a fixed-bed tubular reactor, with an inner diameter of 15 mm and a length of 660 mm, which was loaded with 40.0 ml catalyst. A solution of nitrobenzene in benzyl alcohol (1:10 molar ratio of nitrobenzene to benzyl alcohol) was introduced into the reactor at a flow rate of 0.3 ml/min by use of a syringe pump. Excess benzyl alcohol was used not only as the alkylating reagent but also as the solvent. The temperature in the reaction zone was measured with a thermocouple placed in the center of the tube and regulated by use of a PID cascade controller. The hydrogen pressure in the reaction system was set by use of a hydrogen regulator. The reaction mixture was analyzed by gas chromatography (GC) with a 60 m × 0.32 mm × 0.50 μm SE-30 capillary column. The composition of the reaction mixture was identified by GC–MS (HP-1 capillary column: 30 m × 0.25 mm, 0.2 μm film thickness) with an ion-trap detector.

Results and discussion

Catalyst selection and characterization

The reductive *N*-alkylation of nitrobenzene with benzyl alcohol is depicted in Scheme 1. Aniline is initially obtained by hydrogenation of nitrobenzene. The imine intermediate (*N*-benzylideneaniline) is formed by nucleophilic addition of aniline to benzaldehyde, which is produced by dehydrogenation of benzyl alcohol. *N*-Benzylideneaniline is hydrogenated to yield the desired *N*-benzylaniline.

According to the reported mechanism [33, 34], dehydrogenation of benzyl alcohol to benzaldehyde should be the rate-limiting step. Selection of a suitable catalyst is crucial for this reaction. Because of the dehydrogenation and hydrogenation nature of the reaction, transition metal-based catalysts are often



Scheme 1 Reductive *N*-alkylation of nitrobenzene with benzyl alcohol

Table 1 Reaction of nitrobenzene with benzyl alcohol with a variety of catalysts

Entry	Catalyst	Nitrobenzene conversion (%)	Selectivity (%)	
			N-Benzylaniline	*N*-Benzylideneaniline
1	$Ni_{30}/\gamma\text{-}Al_2O_3$	99.5	70.1	17.2
2	$Co_{30}/\gamma\text{-}Al_2O_3$	99.8	72.7	16.3
3	$Cu_{30}/\gamma\text{-}Al_2O_3$	99.8	77.1	16.4
4	$Cu_{20}/\gamma\text{-}Al_2O_3$	84.3	70.8	16.9
5	$Cu_{10}/\gamma\text{-}Al_2O_3$	53.2	61.7	33.3
6	$Cu_{30}La_5/\gamma\text{-}Al_2O_3$	99.3	84.3	13.6
7	$Cu_{30}Zn_5/\gamma\text{-}Al_2O_3$	98.3	80.6	13.4
8	$Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$	99.9	90.6	7.3
9	$Cu_{30}Mg_5/\gamma\text{-}Al_2O_3$	97.6	83.9	11.3
10	$Cu_{30}Ca_5/\gamma\text{-}Al_2O_3$	99.5	85.1	12.8
11	$Cu_{30}Cr_2/\gamma\text{-}Al_2O_3$	99.7	87.1	8.9
12	$Cu_{30}Cr_{10}/\gamma\text{-}Al_2O_3$	97.5	88.1	7.7

Reaction conditions: temperature = 200 °C, hydrogen pressure = 3.0 MPa, flow rate = 0.3 ml/min, nitrobenzene–benzyl alcohol (mol) = 1:10

used. Because nickel [35, 36] and copper [37–39] have been shown to enable effective *N*-alkylation of amines with alcohols, a series of copper, nickel, and cobalt-based catalysts were prepared and evaluated for reductive *N*-alkylation of nitrobenzene with benzyl alcohol. The results are summarized in Table 1.

GC–MS analysis of the reaction mixture showed the other main product was *N*-benzylideneaniline, *N*,*N*′-dibenzylaniline was not observed. It is apparent that selectivity was much better for $Cu_{30}/\gamma\text{-}Al_2O_3$ than for $Ni_{30}/\gamma\text{-}Al_2O_3$ and $Co_{30}/\gamma\text{-}Al_2O_3$. Copper was therefore chosen as the main catalyst for reductive *N*-alkylation of nitrobenzene with benzyl alcohol. However, the catalytic activity of $Cu_{30}/\gamma\text{-}Al_2O_3$ decreased quickly during the reaction. Shiau and Lee [40] reported that deactivation of $Cu/\gamma\text{-}Al_2O_3$ was caused by sintering of the copper. To improve the stability of the catalyst and selectivity for the desired product, the $Cu/\gamma\text{-}Al_2O_3$ was doped with Cr, La, Zn, Mg, or Ca as second component. As shown in Table 1, the best catalytic performance was obtained with $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$, which was therefore selected as catalyst for synthesis of *N*-benzylaniline. To study the effects of the Cr on the $Cu/\gamma\text{-}Al_2O_3$, $Cu_{30}/\gamma\text{-}Al_2O_3$ and $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$ were studied by XRD, H_2-TPR, and TEM.

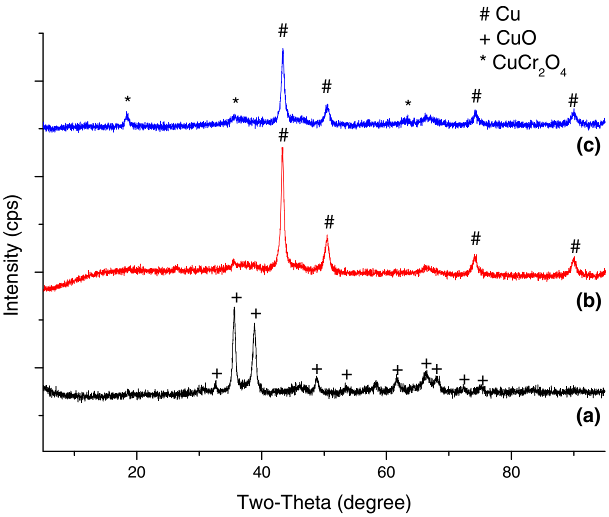


Fig. 1 XRD curves for (*a*) unreduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$, (*b*) reduced $Cu_{30}/\gamma\text{-}Al_2O_3$, and (*c*) reduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

Catalyst characterization

XRD

The XRD patterns for unreduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$, reduced $Cu_{30}/\gamma\text{-}Al_2O_3$, and reduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$ are shown in Fig. 1. As shown by the diffraction lines labeled "+" in Fig. 1a, Cu exists as CuO in the unreduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$. The XRD patterns contained the typical diffraction lines of elemental copper, at 43.3°, 50.4°, 74.2°, and 90.0° in Fig. 1b, c. Cu^0 particle sizes for the (111) diffraction peak (43.3°) were calculated by use of the Scherrer equation. When Cr was doped into $Cu_{30}/\gamma\text{-}Al_2O_3$, the diameter of Cu^0 particles decreased from 243 ± 8 Å in the reduced $Cu_{30}/\gamma\text{-}Al_2O_3$ to 178 ± 6 Å in the reduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$. This indicated that doping with Cr made the Cu particles smaller and better dispersed. XRD peaks of $CuCr_2O_4$ were detected in the reduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$, indicating that addition of Cr may prevent copper from sintering. No peaks corresponding to Cr_2O_3 were identified by XRD, indicating that the particle size of the Cr_2O_3 in the catalyst was either too small to be detected or was present as an amorphous phase.

H_2-TPR

The reducibility of the copper species in the unreduced catalysts was evaluated by H_2-TPR; the results are shown in Fig. 2. The reduction temperature of the main peak shifts from 310 °C for the unreduced $Cu_{30}/\gamma\text{-}Al_2O_3$ to 258 °C for the unreduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$. This result indicated that addition of chromium to $Cu_{30}/\gamma\text{-}Al_2O_3$ can promote the reduction of the catalyst and thus improve the

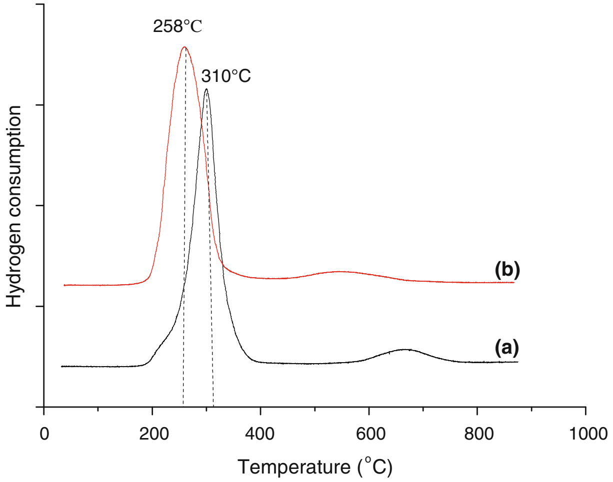


Fig. 2 H_2-TPR curves for (*a*) unreduced Cu_{30}/γ-Al_2O_3 and (*b*) unreduced $Cu_{30}Cr_5/\gamma$-Al_2O_3

dispersion of Cu^0 particles in the catalyst. These results are in good agreement with the XRD results.

XPS

The XPS spectrum of reduced $Cu_{30}Cr_5/\gamma$-Al_2O_3 is shown in Fig. 3. The peak at 932.31 eV, the binding energy of the Cu2p3/2 level, indicates that Cu mainly occurs as Cu^0 species in the reduced $Cu_{30}Cr_5/\gamma$-Al_2O_3 catalyst, as already observed in the XRD pattern of reduced $Cu_{30}Cr_5/\gamma$-Al_2O_3 catalyst. The binding energy of the Cr2p3/2 level at 576.24 eV could be assigned to Cr^{3+}, which occurs as $CuCr_2O_4$. The presence of $CuCr_2O_4$ could be helpful to the dispersion of the Cu^0 species. These results are in agreement with the XRD and H_2-TPR analysis, and it can be concluded that Cu^0 is the active site of the catalyst.

Optimization of the process conditions

Hydrogen pressure

As shown in Scheme 1, hydrogen is involved in the hydrogenation of nitrobenzene to aniline, dehydrogenation of benzyl alcohol to benzaldehyde, and hydrogenation of the imine to the desired product. Thus, the effect of hydrogen pressure on the reaction was investigated; the results are listed in Table 2. When the hydrogen pressure was increased from 1 to 3 MPa, selectivity for *N*-benzylaniline increased from 54.9 to 90.6 %. When the hydrogen pressure was increased further, the selectivity for *N*-benzylaniline decreased. This may be because a hydrogen pressure of 3 MPa was favorable for production of *N*-benzylaniline, by hydrogenation of *N*-benzylideneaniline, whereas higher hydrogen pressure may inhibit the

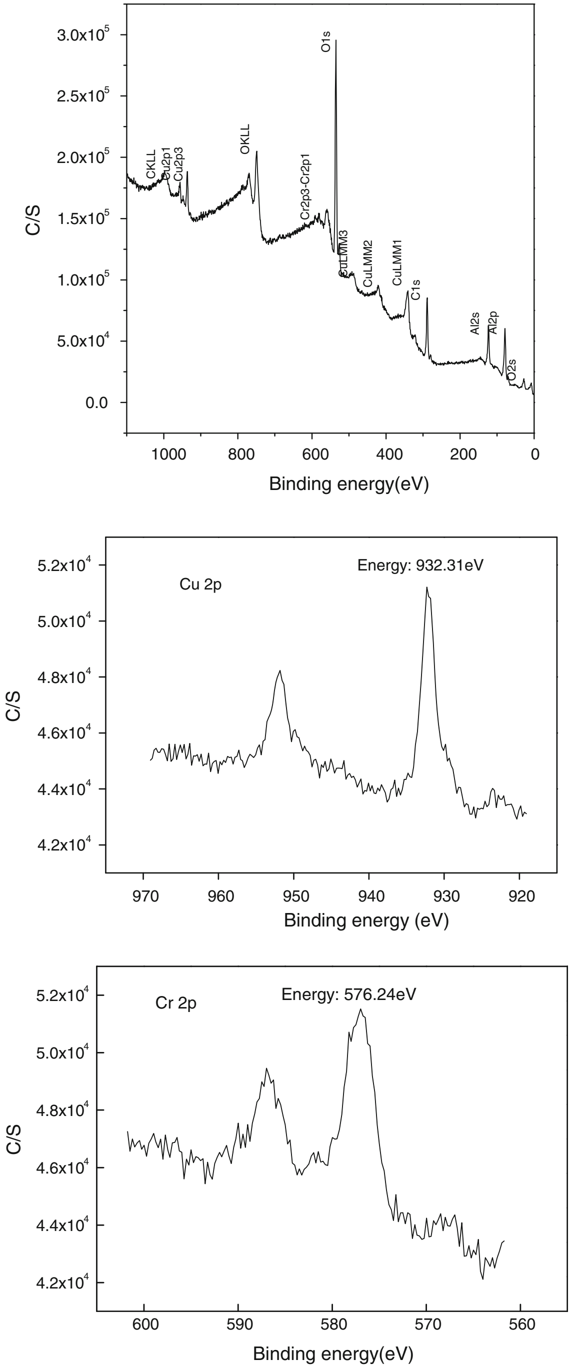


Fig. 3 XPS spectra of reduced $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

Table 2 Effect of hydrogen pressure on the reaction over $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

Hydrogen pressure (MPa)	Nitrobenzene conversion (%)	Selectivity (%)	
		N-Benzylaniline	*N*-Benzylideneaniline
1	99.5	54.9	15.6
2	99.6	81.1	13.3
3	99.9	90.6	7.3
4	99.7	40.1	37.4

Reaction conditions: temperature = 200 °C, flow rate = 0.3 ml/min, nitrobenzene–benzyl alcohol (mol) = 1:10

Table 3 Effect of temperature on the reaction over $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

Temperature (°C)	Nitrobenzene conversion (%)	Selectivity (%)	
		N-Benzylaniline	*N*-Benzylideneaniline
160	99.7	46.8	50.4
180	99.8	86.3	12.1
200	99.9	90.6	7.3
220	99.7	69.7	21.5

Reaction conditions: hydrogen pressure = 3.0 MPa, flow rate = 0.3 ml/min, nitrobenzene–benzyl alcohol (mol) = 1:10

dehydrogenation of benzyl alcohol. Taking the operational feasibility of the process into consideration, 3 MPa was chosen as the optimum hydrogen pressure.

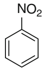
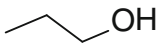
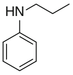
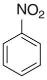
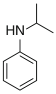
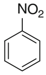
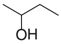
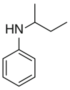
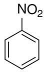
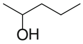
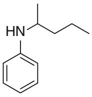
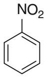
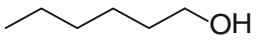
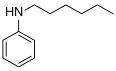
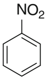
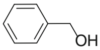
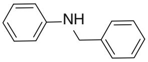
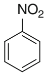
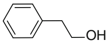
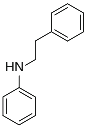
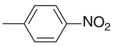
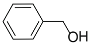
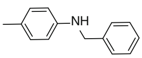
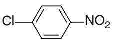
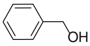
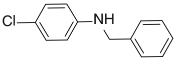
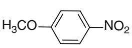
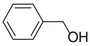
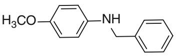
Reaction temperature

The effect of reaction temperature on reductive *N*-alkylation of nitrobenzene with benzyl alcohol over $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$ was examined; the results are shown in Table 3. It is apparent that conversion of nitrobenzene was independent of temperature in the range 160 to 220 °C and remained approximately 100 %. In response to the increasing temperature, selectivity for *N*-benzylaniline increased. The highest selectivity, 90.6 %, was obtained at 200 °C; it decreased to 69.7 % at 220 °C. This indicates that enhancement of the reaction temperature can facilitate dehydrogenation of benzyl alcohol, which led to the more desired product. However, higher temperature may result in formation of the di-alkylated *N*,*N*-dibenzylaniline. Taking the yield of *N*-benzylaniline into consideration, 200 °C was selected as the optimum reaction temperature.

Reductive N-alkylation of nitrobenzenes and different alcohols over $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

The scope of this $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$-catalyzed system with regard to nitrobenzene derivatives and alcohols was examined; the results are summarized in Table 4. The

Table 4 Reductive *N*-alkylation of nitrobenzenes with different alcohols over $Cu_{30}Cr_5/\gamma\text{-}Al_2O_3$

Entry	Nitroaromatics	Alcohols	Product	Temperature (°C)	Yield (%)
1				180	93.4
2				200	95.6
3				200	96.4
4				200	95.1
5				180	90.8
6				200	90.6
7				200	92.1
8				220	92.7
9				220	94.6
10				220	90.5

Reaction conditions: hydrogen pressure = 3.0MPa, flow rate = 0.3ml/min, nitroaromatic–alcohol (mol) = 1:10

stability of imine and steric bulkiness on the amino group of aniline substantially affected the yield of the product. Reaction of nitrobenzene with aliphatic secondary alcohols proceeded in excellent yields (Table 4, entries 2–4). Because higher temperature could give the undesired di-alkylated anilines, a lower temperature was required when linear alkyl alcohols, for example *n*-propanol and *n*-hexanol, were used as the alkylating agents (Table 4, entries 1 and 5). Aromatic primary alcohols, including benzyl alcohol and 2-phenylethanol, could be transformed into the corresponding product in high yields (Table 4, entries 6 and 7). Furthermore, under the optimized reaction conditions, different 4-substituted nitrobenzenes were benzylated in good yields to give secondary amines (Table 4, entries 8–10).

Lifetime of $Cu_{30}Cr_5/\gamma$-Al_2O_3

Because reductive *N*-alkylation of nitrobenzenes with alcohols had proceeded well in a fixed-bed reactor, the lifetime of the catalyst was measured under the optimum conditions over 150 h. During this period, the stability of the catalyst was good and the yield of *N*-alkylated anilines remained above 85 %. The catalyst had general applicability in the reductive *N*-alkylation of nitrobenzenes with a variety of alcohols.

Conclusion

A facile and efficient method for reductive *N*-alkylation of nitrobenzenes with alcohols over $Cu_{30}Cr_5/\gamma$-Al_2O_3 catalyst in a fixed-bed reactor was successfully established. Cu^0 species were assumed to be the active sites of the catalysts, and doping of Cu_{30}/γ-Al_2O_3 with chromium led to highly dispersed Cu^0 particles. The catalyst system is highly stable and yields are high in the reductive *N*-alkylation of nitrobenzenes with a variety of aliphatic and aromatic alcohols.

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