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Room Temperature N-Alkylation of Amines with Alcohols under UV Irradiation Catalyzed by Cu-Mo/TiO_2

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It is highly desirable to develop efficient heterogeneous photocatalysts for organic reactions. Here, we show the preparation and catalytic performance of a novel TiO_2 (P25) supported Cu and Mo photocatalyst (Cu-Mo/TiO_2) for N-alkylation of amines with alcohols under UV irradiation at room temperature. A variety of aromatic and aliphatic amines were selectively converted into the corresponding secondary amines or tertiary amines in moderate to excellent yields without the addition of any co-catalysts such as bases and organic ligands. Noteworthy, this catalytic system is feasible in the alkylation of anilines containing halogen substituents with alcohols and the yields of the desired products are up to 95%.

Introduction

Nitrogen-containing compounds, particularly amines and their derivatives are important intermediates and products for pharmaceuticals, agrochemicals, polymers, bioactive compounds, and dyes[1-5]. There are several methods to produce them, including amination of aryl/alkyl halides[2, 6], and reductive amination of carbonyl compounds [7, 8]. However, these methods suffer from the drawbacks of the use of a stoichiometric amount of detrimental and/or expensive reagents and the formation of a large amount of noxious side products. In recent years, much attention has been focused on development of catalytic methods for the production of N-alkylated amines applying alcohols as alkylating agents because alcohols are nontoxic, plentiful, inexpensive and renewable feedstock regents.

Initially, the N-alkylation of amines with alcohols was carried out in the presence of various kinds of homogeneous transition-metal catalysts including ruthenium[9-11], platinum[12], iridium[13-18], silver[19] and palladium[20, 21] complexes with which good results were obtained. Later on, some heterogeneous catalysts such as Pd/MgO[22], Ag/Mo[23] or Ag/Al_2O_3[24], Cu-Ag/Al_2O_3[25], Au/TiO_2[26], $Cu(OH)_2$/Al_2O_3[27], Ni/Al_2O_3[28], Cu/Ni-based[29], Ni-Cu/Al_2O_3[30] and Fe_3O_4[31], were developed for the N-alkylation of amines. However, it is still extremely challenging to require harsh reaction conditions such as high temperature and strong base or using noble metal.

The development of more green and economic processes for the N-alkylation of amines with alcohols is crucial subject imposed on organic chemistry. Semiconductor photocatalysis has attracted much attention in the past decades owing to its application in environmental purification[32], water splitting for the generation of hydrogen as a fuel[33], and conversion of solar energy into electrical energy[34], etc. However, the application of semiconductor photocatalysts as a synthetic methodology is less common because semiconductor photocatalytic reactions have often been considered as highly unselective processes, especially in water[35]. We have been particularly interested in using semiconductor photocatalysts as a new way to drive chemical reactions for organic synthetic transformations with high activity and selectivity, such as the reaction of N-alkylation of amines with alcohols. So far, several semiconductor photocatalysts have been reported, inclusive of Pt/TiO_2[36, 37], Au/TiO_2[38] and Pd/TiO_2[39, 40], which use noble metal catalysts. However, there is no report of active and general non-noble metal catalyst for this transformation. The development of non-noble metal semiconductor photocatalyst is highly desirable.

Herein, we report our results about Cu-Mo/TiO_2 catalyzed reaction of amine with alcohol under UV irradiation at room temperature. To the best of our knowledge, this is the first non-noble metal supported semiconductor photocatalyst for the N-alkylation of amines with alcohols. Notably, our catalytic system is also suitable for the alkylation of anilines with halogen group and the dehalogenation reaction can be inhibited efficiently under UV light irradiation.

Results and Discussion

Catalyst characterization. The catalysts used in this work were prepared by the precipitation-deposition method and followed by reduction with $NaBH_4$ solution. The textual property of the catalysts was characterized by N_2 adsorption-desorption method. The results of BET surface area, pore volume and pore size of TiO_2 and Metal/TiO_2 (M/TiO_2) samples were given in Table 1. The BET surface area of M/TiO_2 samples was slight larger than TiO_2. The pore volume and pore size for M/TiO_2 samples were similar, but twice as much as TiO_2. According to the ICP-AES analysis, the copper loadings in Cu/TiO_2 and Cu_1-Mo_1/TiO_2 were 0.853 wt% and 0.854 wt%, respectively. However, only 0.002-0.003 wt% molybdenum existed in Mo/TiO_2 and Cu_1-Mo_1/TiO_2.

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Table 1. BET surface area, pore volume, pore size and metal loadings of typical catalysts

Catalysts	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size(nm)	Cu content (wt%)	Mo content (wt%)
TiO_2	49	0.103	8.45	-	-
Mo/TiO_2	56	0.228	16.39	-	0.003
Cu/TiO_2	51	0.224	17.54	0.853	-
Cu_1-Mo_1/TiO_2	55	0.214	15.51	0.854	0.002

The crystal structures of all samples in our study were characterized by XRD measurement, as show in Figure 1. The peaks marked "A" and "R" refer to anatase and rutile phases, respectively. All catalysts showed identical mixed phases of anatase and rutile TiO_2 without appearance of metal oxide or metal particles, which might be ascribed to the low metal loadings and the good dispersion of metal species on the surface of TiO_2. The morphology of the Cu_1-Mo_1/TiO_2 and Cu_1-Mo_3/TiO_2 samples was examined by TEM and high resolution TEM (HR-TEM) in Figure 2. It is clear that the photocatalysts were almost composed of TiO_2 which have different shapes and sizes because of including two phases (anatase and rutile). No obvious Cu species particles were observed on the two samples. The possible reason for the observation was that at the low loading, the small Cu particles highly dispersed on the surface. This was in good agreement with the results of the XRD analysis shown in Figure 1.

XPS was used to analyze the chemical state and composition of surface elements in the catalysts. Figure 3a shows the Ti2p XPS profiles for TiO_2, Cu_1-Mo_1/TiO_2, Mo/TiO_2 and Cu/TiO_2. The peaks of $Ti2p_{1/2}$ and $Ti2p_{3/2}$ for all samples were observed at ~458.8 and ~464.3 eV. This indicated the presence of TiO_2 in the form of Ti^{4+} ions[41-43]. The positions of Ti2p peaks for other catalysts don't show significant difference compared to the bare TiO_2, but a decrease in intensity of Ti2p peaks is observed for Cu_1-Mo_1/TiO_2 and Cu/TiO_2, implying that Ti^{4+} is partially transformed into Ti^{3+}, which is widely accepted as having higher photocatalytic activity[43, 44].

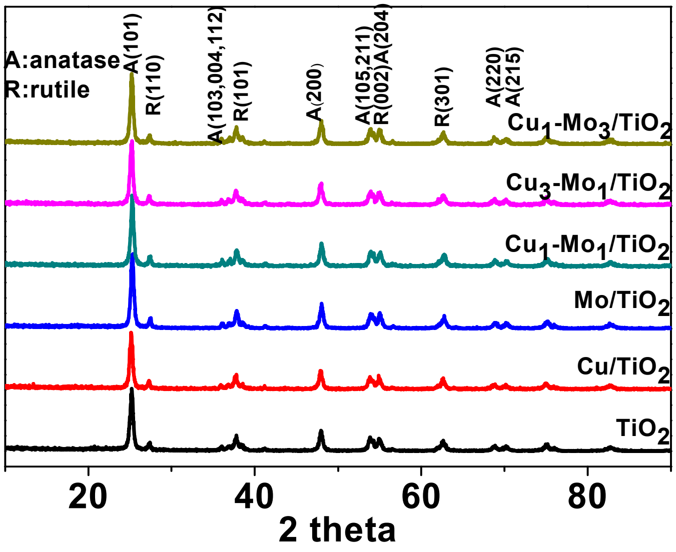

Figure 1. XRD diffraction patterns of the catalyst samples

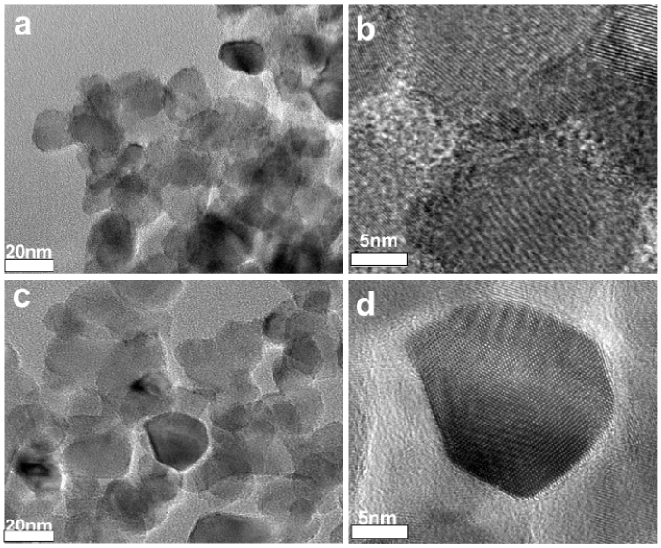

Figure 2. TEM and HR-TEM images of Cu_1-Mo_1/TiO_2 (a and b) and Cu_1-Mo_3/TiO_2 (c and d).

Figure 3b is the Cu2p XPS spectra for Cu_1-Mo_1/TiO_2 and Cu/TiO_2. The XPS spectra of Cu_1-Mo_1/TiO_2 displays two main peaks at 932.7 and 952.4 eV, that can be attributed to the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ binding energies[45], respectively. The XPS spectra indicate the possible presence of Cu^0 or Cu^{+}[45, 46]. In order to verify the chemical state of copper species, Cu_{LMM} peaks were collected and were shown in Figure S1. A peak at 921.7eV, which should be assigned to Cu^0, and a smaller peak at 914.8 eV, which can be attributed to Cu^+, are observed[47-49]. Therefore, both Cu^+ and Cu^0 were contained in the catalyst. In addition, a peak ($Cu2p_{1/2}$ at 954.1 eV) and a satellite peak (at 942.0 eV) for characteristic Cu^{2+} are also observed[50, 51]. The appearance of metallic Cu is due to the reduction of Cu^{2+} to Cu^0 during catalyst preparation (reduction with $NaBH_4$ solution). The Cu^{2+} exists in Cu_1-Mo_1/TiO_2 on account of the generation of Cu copper oxide in the air. In contrast, the Cu2p peaks for Cu^0 are observed in Cu/TiO_2, but the Cu2p peaks related to copper oxide are very weak. Figure 3c presents the O1s spectra of the samples. The O1s spectra are composed by two peaks whose binding energies are 530 eV (Ti-O) and 532.2 eV (Ti-OH)[43, 46]. The peaks of the O1s spectra in Mo/TiO_2 move to remarkably lower binding-energy levels if compared to the values of TiO_2. The positions of the O1s peaks of Cu_1-Mo_1/TiO_2 show slight shifts toward lower binding-energy and a decrease in intensity is also observed. In sample Cu/TiO_2, the intensity of the O1s peaks at 532.2 eV becomes stronger and the other peak at 530 eV is weaker compared with TiO_2. The Mo3d spectra of Mo/TiO_2 and Cu_1-Mo_1/TiO_2 samples are shown in Figure 3d. No Mo3d peaks were observed in the two catalysts due to the low concentration of Mo on the surface.

As a sensitive technique, Raman spectroscopy has been used to investigate the phase composition and surface homogeneity. Figure 4 shows the Raman spectra of different catalysts. There are five Raman peaks at 142, 196, 395, 515 and 636cm-1 for all the samples, corresponding to E_g, E_g, B_{1g}, A_{1g} and E_g modes of anatase phase of TiO_2[52, 53], respectively. It indicates that anatase TiO_2 nanoparticles are the predominant species. Furthermore, there are no characteristic peaks corresponding to Cu or Mo species were found in the samples, which is consistent with the results of XRD diffraction patterns. The Raman peaks at E_g of 142 cm^{-1} and those at B_{1g} of 395 cm^{-1} are O-Ti-O bending-type

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vibrations, and the peaks at E_g of 636 cm^{-1} and those at A_{1g} of 515 cm^{-1} are the Ti-O bond stretching-type vibrations[54].

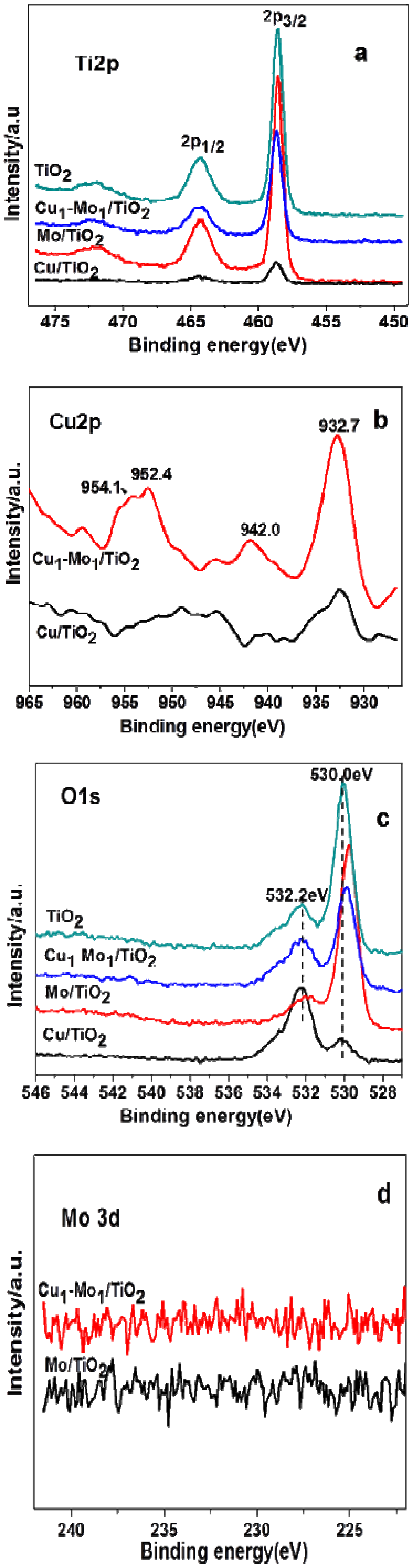

Figure 3. Ti2p (a), Cu2p (b), O1s (c) and Mo3d (d) XPS spectra of the catalyst samples

As shown in Fig. 4, the peaks of Mo/TiO_2, compared to the peaks of bare TiO_2, have stronger intensity. It is also found that the peaks of Cu_1-Mo_1/TiO_2 are stronger than Mo/TiO_2. However, some peaks of Cu/TiO_2 almost disappear.

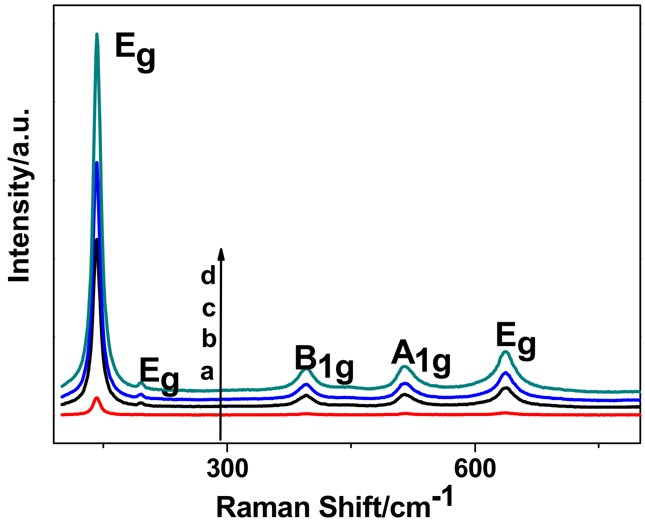

Figure 4. Raman spectra of (a) Cu/TiO_2 ,(b) TiO_2, (c) Mo/TiO_2 and (d) Cu_1-Mo_1/TiO_2

To compare the optical responses of the synthesized photocatalysts, their diffuse reflectance UV-vis absorption spectra are determined and are shown in Figure 5. All samples exhibit a wide optical absorption in the range below 400 nm. It is apparent that the diffuse reflectance spectra of Mo/TiO_2 and Cu/TiO_2 have a red shift in comparison with TiO_2. However, the absorption edge of Cu_1-Mo_1/TiO_2 is observed to be blue-shifted, which may be attributed to the quantum-size effect[55, 56]. Co-modifying with Cu and trace Mo is shown to induce the band gap of TiO_2 broadening. This result suggests that Cu and trace Mo have a synergistic effect on the photo-catalytic activity of TiO_2[52].

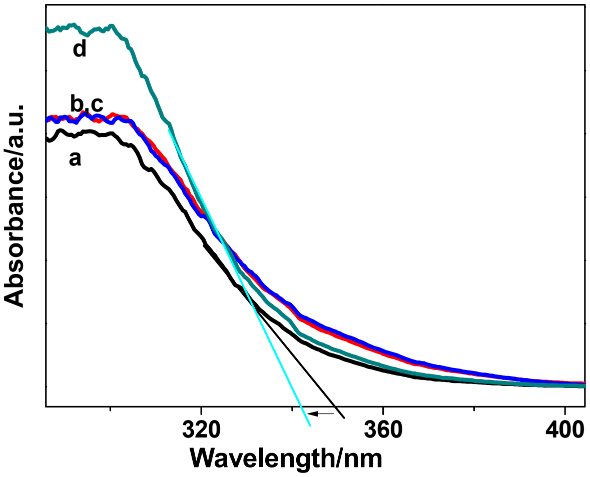

Figure 5. UV-visible absorbance spectra of (a) TiO_2, (b) Cu/TiO_2, (c) Mo/TiO_2 and (d) Cu_1-Mo_1/TiO_2

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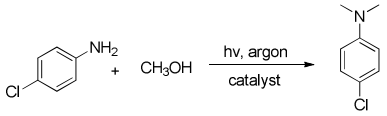
Catalytic N-alkylation reactions. Following, we continued to test the activity of the catalysts in N-alkylation of amines with alcohols at room temperature under UV irradiation. In the case, *p*-Cl-aniline and methanol were used as model substrates. The corresponding results were summarized in Table 2. First, TiO_2 without any modification was used as catalyst and no desired product was obtained (Entry 1). Then, the reaction was carried out in presence of Mo/TiO_2, unfortunately, there was also no desired product formed (Entry 2). Following, when the reaction was conducted using Cu/TiO_2 as catalyst, only 19% yield was obtained (Entry 3). These results indicated that the TiO_2 itself and Mo/TiO_2 are inactive for the N-alkylation reaction of amine under our reaction conditions. Although the yield is not high, Cu/TiO_2 as the catalyst was efficient for this transformation. In order to get a more effective catalyst, we tried to apply Cu and Mo together to modify TiO_2. By adjusting the Cu/Mo molar ratio, three catalysts were obtained and used in the N-alkylation reaction and the highest yield, i.e., 95%, was obtained when the Cu/Mo molar ratio was 1 : 1. If the Cu/Mo molar ratios were varied to 3 : 1 and 1 : 3, the yields were 29% and 13%, respectively (Entries 4-6). The light intensity also remarkably influences the reaction. An excellent yield, i.e. 95%, was obtained if using Cu_1-Mo_1/TiO_2 as catalyst under irradiation of 100% light intensity (245 mW/cm^2, entry 5). The yield was only 5% when the light intensity was decreased to 60%, and no desired product was observable if the light intensity was further decreased to 30% (Entries 7 and 8). In addition, a self-prepared TiO_2 was used as the support for catalyst preparation but lower activity was obtained (Entry 9).

Table 2. Catalyst screening and reaction conditions optimization using N,N-dimethylation of p-chloroaniline reaction[a]

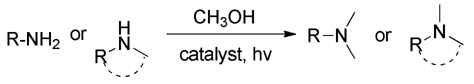


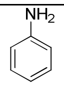
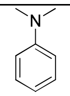
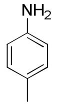
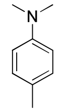
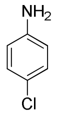
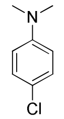
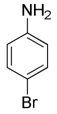
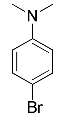
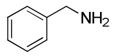
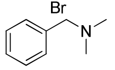
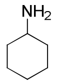
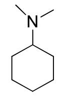
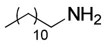
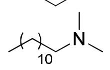
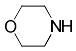
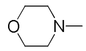
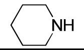
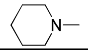
Entry	Catalyst	Conversion%	Yield%[b]
1	TiO_2	100	0
2	Mo/TiO_2	100	0
3	Cu/TiO_2	100	19
4	Cu_3-Mo_1/TiO_2	100	29
5	Cu_1-Mo_1/TiO_2	100	95[c]
6	Cu_1-Mo_3/TiO_2	100	13
7	Cu_1-Mo_1/TiO_2	100	5[d]
8	Cu_1-Mo_1/TiO_2	100	0[e]
9	Cu_1-Mo_1/TiO_2-SP	100	4[f]

[a] Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg), argon, UV (365 nm LED, 245 mW/cm^2), r.t., 21 h. [b] The yields were obtained by GC-FID using biphenyl as external standard material. [c] Isolated yield. [d] 60% light intensity. [e] 30% light intensity. [f] TiO_2 was prepared in our laboratory.

With this optimized reaction condition in hand, we next proceeded to examine the scope of the Cu_1-Mo_1/TiO_2 catalyst in the N-alkylation reaction of amines with alcohols. First, the catalytic protocol was extended to the N-alkylation reaction of amines with methanol and the results were listed in Table 3. Aromatic amines, including aniline, *p*-methylaniline, *p*-chloroaniline and *p*-bromoaniline, could be transformed into the corresponding N-methyl tertiary amines with 46 to 95% yields (Entries 1-4). Aliphatic amines, such as benzylamine, cyclohexylamine and dodecanamine, could be used as starting materials for the N-methylation reaction, too, and excellent yields of the corresponding tertiary amines were achieved (Entries 5-7). The use of cyclic aliphatic secondary amines including morpholine and piperidine as substrates gave good yields of the desired products, from 82 to 85% (Entries 8-9).

Table 3. N-methylation of amines with methanol[a]



Entry	Amines	Products	Yield%[b]
1			46
2			70
3			95[c]
4			80[c]
5			85
6			94
7			94[c]
8			82
9			85

[a] Reaction condition: amine (0.2 mmol), methanol (5 mL), Cu_1-Mo_1/TiO_2 (20 mg), argon, UV (365 nm LED, 245 mW/cm^2), r.t., 21 h. [b] The yields were obtained by GC-FID using biphenyl as external standard material. [c] Isolated yields.

Subsequently, N-alkylation reactions of amines with different alcohols were investigated. As shown in Table 4, a variety of primary amines were smoothly alkylated with various aliphatic alcohols affording the corresponding N-alkylated secondary or tertiary amines with good to excellent yields. Interestingly, the chain length of alcohol had significant influence on the reaction (Entries 1-4). When ethanol and 1-propanol were used, the N,N-dialkylation occurred and the yields of products were 80-83% (Entries 1-2). When the reactions were carried out in 1-butanol and 1-hexylalcohol, the N-monoalkylation products were obtained in high yields (Entries 3-4). The transformation of *p*-bromoaniline with different alcohols afforded the similar results. The corresponding products were obtained in 95 and 65% yield (Entries 5-6), respectively. 4-Toluidine and 4-anisidine reacted with 1-propanol to give alkylated products in moderate yields under the same conditions (Entries 7-8). The catalyst also showed good activity towards the alkylation of aniline with two substituted groups. 3,5-Dimethylaniline was alkylated by using 1-propanol and 1-butanol to give secondary amines in good to excellent yields (Entries 9-10). We found that 5-aminoindan was also transformed into the corresponding N-alkylated secondary or tertiary amines in moderate to excellent yields (Entries 11-13). The reactions of aniline with longer alkyl chain

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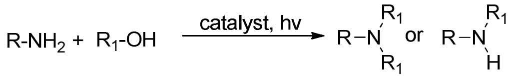
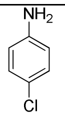
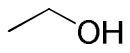
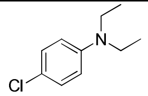
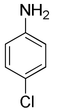
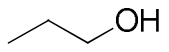
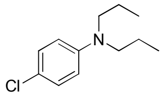
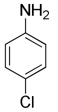
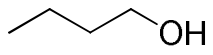
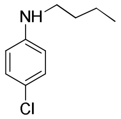
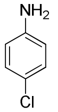
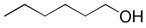
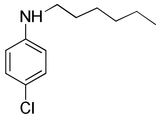
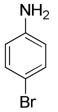
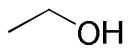
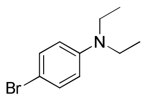
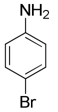
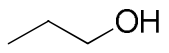
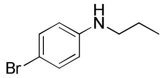
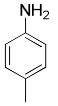
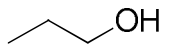
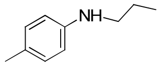
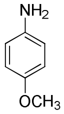
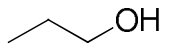
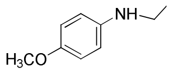
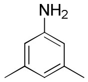
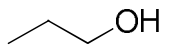
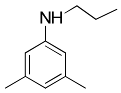
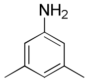
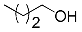
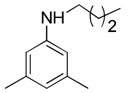
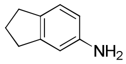
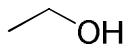
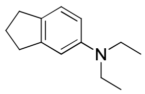
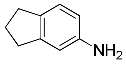
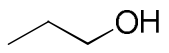
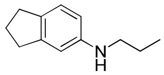
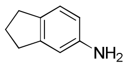
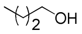
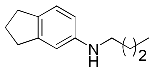
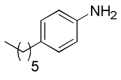
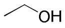
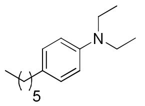
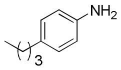
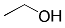
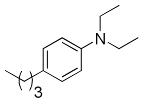
group, such as 4-hexylaniline and 4-butylaniline, and ethanol were investigated. To our delight, N-alkylated products were afforded in 83 and 95% yield (Entries 14-15). 3-Isopropylaniline and 4-tert-butylaniline could also react smoothly to generate the corresponding amines in good yields (Entries 16-17). In addition, our catalytic system was also suitable for alkylation of aliphatic amines. For example, the reaction of dodecanamine with ethanol and 1-propanol gave the corresponding products in 90 and 81% yields (Entries 18-19), respectively. Finally, almost no N-alkylation product was observed if benzyl alcohol was used in the N-alkylation reaction of *p*-chloro-aniline. Therefore, this catalyst is active for the N-alkylation of amines with aliphatic alcohols but not active for the amination reaction of aromatic alcohols.

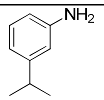
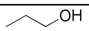
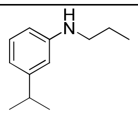
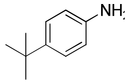
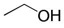
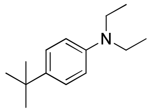
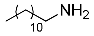
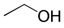
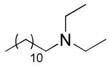
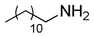
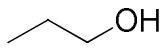
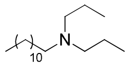
The proposed reaction mechanism. After the successful alkylation of amines with different alcohols, we were further interested in the reaction mechanism. Therefore, the reactions of *p*-chloroaniline with methanol and ethanol were traced by GC-MS to check the possible reaction intermediates, respectively. Interestingly, the two reactions have similar intermediates, i.e., imines, in the process of secondary amines generation, however, completely different reaction intermediates are formed during the production of tertiary amines. Methoxy hemiaminals as intermediates are formed during the generation of trimethyl amine in the N-methylation reaction via the addition of methanol to iminium ion. This intermediate is not observed in the N-ethylation reactions of amines. (Figure 6(A)). The time-dependent change in quantity variations of the intermediates were shown in Figure 6. In Figure 6 (B), almost all the *p*-chloroaniline was consumed at the initial stage and the possible product was *p*-chloro-N-ethylideneaniline via condensation of *p*-chloroaniline with acetaldehyde, which was produced by the dehydrogenation of ethanol. As the amount of *p*-chloro-N-ethylideneaniline and *p*-chloro-N-ethylaniline reduced fast, we supposed that *p*-chloro-N-ethylideneaniline was hydrogenated to *p*-chloro-N-ethylaniline and *p*-chloro-N-ethylaniline will react with ethanol again, and *p*-chloro-N,N-diethylaniline was produced[57]. Similar results were obtained if the addition reaction of methanol and iminium ion could not proceed.

On the basis of the above results, two main pathways can be proposed for the alkylation of amines with alcohols in our catalytic system, and they are illustrated in Figure 7. (1) As pathway A showed, the photocatalytic activity is improved in the UV-light region. During the N-methylation reaction, the electron and hole pairs formed in TiO_2, by UV-light irradiation, migrate to catalyst surface to react with absorbed substrates. The hole oxidizes methanol to formaldehyde and H^+ in presence of CuO_x. H^+ is reduced on the surface of Cu^0 by the electron transferred from the TiO_2 conduction band and produces the Cu-hydride species (Cu-H)[58]. Parts of the H atoms are removed from the surface Cu^0 by coalescence as H_2 gas[39]. The imine is generated by condensation of the formed formaldehyde with *p*-chloroaniline by the Lewis acid site on the TiO_2 surface[59]. Next, the imine is hydrogenated by Cu-H species and is transformed to *p*-chloro-N-methylaniline. Then, iminium ion is generated by condensation of *p*-chloro-N-methylaniline with formaldehyde[60]. There are two stages to transform the iminium ion. At the initial stage, iminium ion preferentially reacts with methanol to generate methoxy hemiaminals, which are thermodynamically less stable and serves as a resting state for iminium ion[61, 62]. In the second stage, the iminium ion is immediately reduced by Cu-H species and *p*-chloro-N,N-dimethylaniline is generated. (2) A conventional reductive reaction of iminium ion with

Table 4. N-alkylation of amines with alcohols[a]



Entry	Amines	alcohols	Products	Yield%[b]
1				80
2				83
3				90
4				93
5				95
6				65
7				60
8				70
9				94
10				91
11				80
12				78
13				87
14				95
15				83

16				88
17				85
18				90
19				81

[a]Reaction condition: amine (0.2 mmol), alcohol (5 mL), Cu_1-Mo_1/TiO_2, (20 mg), argon, UV (365 nm LED, 245 mW/cm^2), r.t., 21 h. [b]Isolated yield.

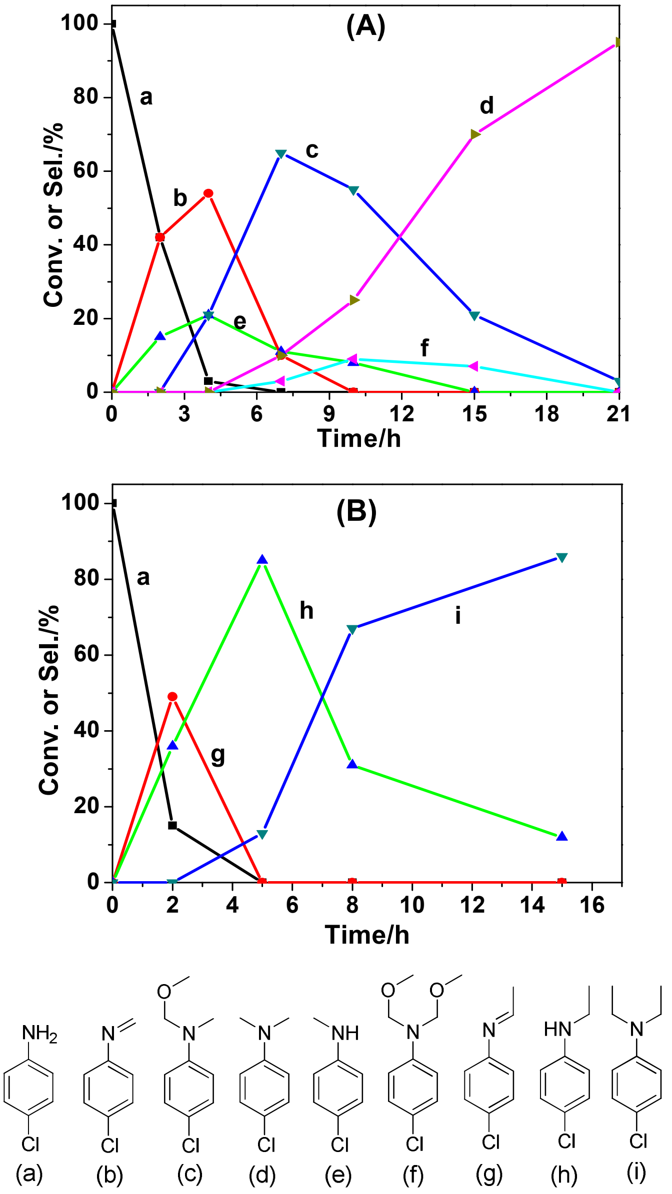


Figure 6. Time-dependent variation of substrates and products during photoreaction of p-chloroaniline with (A) methanol and (B) ethanol catalyzed by Cu_1-Mo_1/TiO_2. Reaction conditions: see Table 3 and Table 4.

Cu-H species is smoothly performed in ethanol and *p*-chloro-N,N-diethylaniline is gained. Excepting for methanol, hemiaminal intermediates were not detected during the investigation of *p*-chloroaniline with ethanol (Figure 6 (B)). Therefore, the pathway B is suitable for the alkylation of amines with other alcohols under the present reaction condition. Noteworthy, although different catalytic activities were observed when catalysts with different Cu/Mo ratios were applied, they should take the same reaction pathways due to the similar reaction intermediates observed by GC-MS.

Conclusions

In summary, we have developed a convenient and straightforward photocatalytic system for the N-alkylation of amines using alcohols as solvent and reactant. A series of photocatalysts, which are TiO_2 decorated with non-noble metal copper and molybdenum (Cu-Mo/TiO_2), were prepared through a simple procedure using commercially available TiO_2. By applying this catalyst, various secondary and tertiary amines are successfully synthesized with high yields at room temperature under UV irradiation. This photocatalytic system offers significant advantages including broad substrate scope, no harmful byproduct formation, simple procedure and environmentally benign, which make it an attractive method for N-alkyl amine synthesis.

Acknowledgements

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Experimental Section

Typical procedure for catalyst preparation: MoO_3 (12 mg) was dissolved with stirring in 1 M NaOH (1 mL) at room temperature until the complete dissolution of MoO_3, then deionized water (30 mL) was added. Following, TiO_2 (0.5 g, P25, J&K Scientific, anatase/rutile =80/20, BET surface, 35-65 m^2/g) was dispersed in the solution and $CuCl_2$ aqueous solution (14 mg/5 mL deionized water) were added into the solution under vigorous stirring. After the addition of $CuCl_2$ was completed, the solution was stirred for another 3 h at room temperature. Then $NaBH_4$ (20 mg/3 mL deionized water) was added to the solution in ice water bath and stirred for 2 h. The solid sample was recovered by centrifugation and washed with deionized water (40 mL × 2). The obtained solid was dried at 80 ^{o}C, and was denoted as Cu_1-Mo_1/TiO_2. Cu_1-Mo_3/TiO_2 and Cu_3-Mo_1/TiO_2 were prepared with the same procedure but 7 mg $CuCl_2$/18 mg MoO_3 or 21 mg $CuCl_2$/6 mg MoO_3 were used.

Typical reaction procedure: amine (0.2 mmol), catalyst (20 mg) and alcohol (5 mL) were added into a glass tube (35 mL). Argon was bubbled through the solution for 5 min. Then the tube was sealed with a rubber cap and photoirradiated by a LED light (365 nm, 245 mW/cm^2) with magnetic stirring at room temperature for 21 h. Subsequently, 10 mg biphenyl and 5 mL ethanol were added for quantitative analysis by GC-FID

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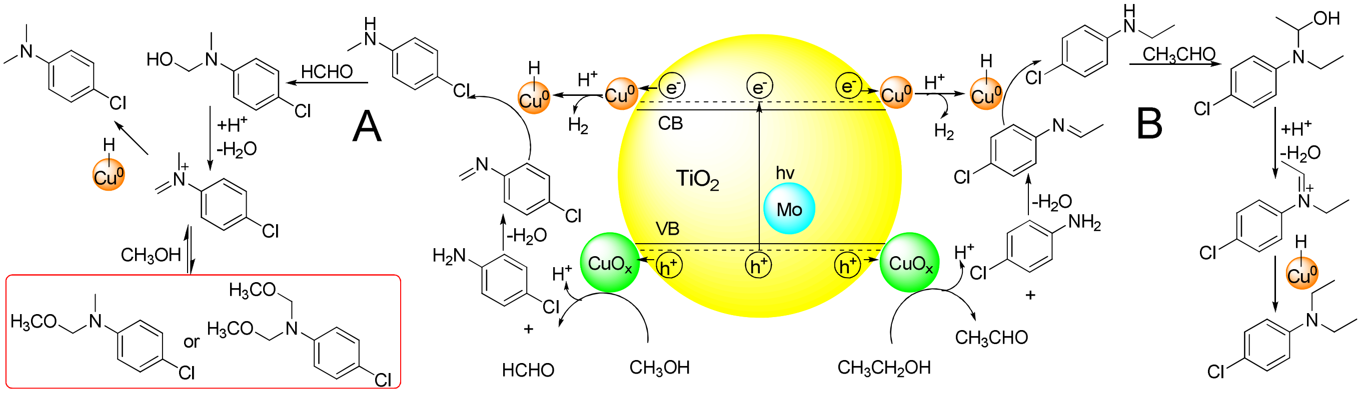

Figure 7. Proposed reaction mechanism for light promoted N-alkylation of *p*-chloroaniline over Cu-Mo/TiO_2

(Agilent 6890A) and some products were purified by vacuum distillation after removing the catalyst by filtration or flash column chromatography.

Catalyst characterization: Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. XRD measurements were conducted by an X'Pert PRO (PANalytical) diffractometer. The XRD diffraction patterns were scanned in the 2θ range of 10-90°. TEM analysis was carried out with a FEI-TF20 field emission transmission electron microscope. The XPS measurements were performed with a ESCALAB 210 instrument provided with a dual 15 Mg/Al anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar^+ ion-gun. The Raman measurements were carried out with a Renishaw inVia Raman microscope at room temperature. Diffuse reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (UV-2550 (Shimadzu)) with BaSO4 as a reference at room temperature. The Cu and Mo loadings were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an Iris advantage Thermo Jarrel Ash device. The Cu loadings in catalysts

Notes and references

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† Electronic Supplementary Information (ESI) available: characterizations of the products. See DOI: 10.1039/b000000x/

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Room Temperature N-Alkylation of Amines with Alcohols under UV Irradiation Catalyzed by Cu-Mo/TiO$_2$

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Cu-Mo/TiO$_2$ can be an activephotocatalyst for N-alkylation of amines with alcohols under UV irradiation at room temperature without the addition of noble metals.