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Light-promoted *N,N*-dimethylation of amine and nitro compound with methanol catalyzed by Pd/TiO₂ at room temperature†

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A series of TiO₂ supported nano-Pd catalysts (Pd/TiO₂) were prepared and used for the *N,N*-dimethylation of different amines and nitro compounds with methanol under UV irradiation at room temperature. A wide range of *N,N*-dimethyl amines were one-pot synthesized with up to 98% by applying aliphatic secondary amines, aromatic primary amines, aliphatic primary amines and aromatic nitro compounds as starting materials. It is noteworthy that up to 90% yield of 4-chloro-*N,N*-dimethylaniline was obtained by adjusting the Pd loadings on the TiO₂ and the dehalogenation reaction was inhibited. Finally, a reaction mechanism is discussed, involving PhN = CH₂ and PhNHCH₃ as reaction intermediates.

Introduction

N-Methyl and *N,N*-dimethyl amines are important materials in the fields of pharmaceuticals, dyes, paints and agriculture.^{1–5} Compared with other *N*-alkyl amines, *N*-methyl and *N,N*-dimethyl amines have attracted extensive attention in industry. Generally, they are mainly synthesized through three pathways: (1) reaction of amines with methylating reagents such as methyl halides, dimethyl sulfate,⁶ dimethyl carbonate,⁷ dimethyl sulfide (DMSO)⁸ and so on; (2) reductive amination reaction of formaldehyde^{9–11} and (3) *N*-methylation of amines with carbon dioxide and molecular hydrogen.^{12–14} Unfortunately, these methods are often problematic from synthetic or environmental standpoints. For example, some processes require harsh reaction conditions such as high temperature or high pressure, the methylating reagents such as methyl halides, dimethyl sulfate and formaldehyde are toxic and very harmful to environment, or large amounts of waste water and inorganic salts are produced. Recently, considerable attentions had been paid on the *N*-alkylation of amines with alcohols as the alkylation reagents.^{15–20} Obviously, alcohols are readily available, cheap, non-toxic, ease of handling, and water is the only by-product theoretically. Hence, the reaction is green and eco-friendly and it provides an alternative route for *N*-methylation of amines. A few catalytic systems^{21–24} have been specially developed for the *N*-methylation of amines and nitro compounds using CH₃OH as

methylating reagent but they still require high temperatures and high pressures. Moreover, these methods were limited to the poor generality or specific catalytic activity for specific amines.

Heterogeneous photo-catalysis with semiconductor as catalyst is an unconventional technology which has traditionally been used in environmental remediation²⁵ and water splitting for the generation of hydrogen.²⁶ Recently, the application of heterogeneous photo-catalysts in synthetic chemistry has been reported and nice results were obtained.^{27–34} To the best of our knowledge, there are a few reports about heterogeneous photo-catalysis in *N*-alkylation of amines,^{35–38} in which only two systems concerning the *N*-methyl and *N,N*-dimethyl amines synthesis. They are Pt particles supported on TiO₂ (anatase)³⁵ and Au particles supported on TiO₂ (P25).³⁸

In these works, five *N*-methylation reactions were concerned and the corresponding results were given in Scheme 1. Clearly, high yields were obtained in the *N*-methylation reaction of *N*-methyl aniline and piperidine. However, poor results were obtained when aniline, benzyl amine and butyl amine were used as the starting materials. Therefore, the development of a new catalyst system for *N,N*-dimethylation of amine and methanol with good generality under mild conditions is highly desirable. In this study, we report a new heterogeneous photo-catalyst system for the synthesis of *N,N*-dimethyl amines, *i.e.* Pd/TiO₂. By applying this catalyst, amines and nitro compounds with different structures can react with methanol, which acts both as solvent and reactant, at room temperature smoothly. Noteworthy, the methanol can be easily recovered and recycled after reaction.

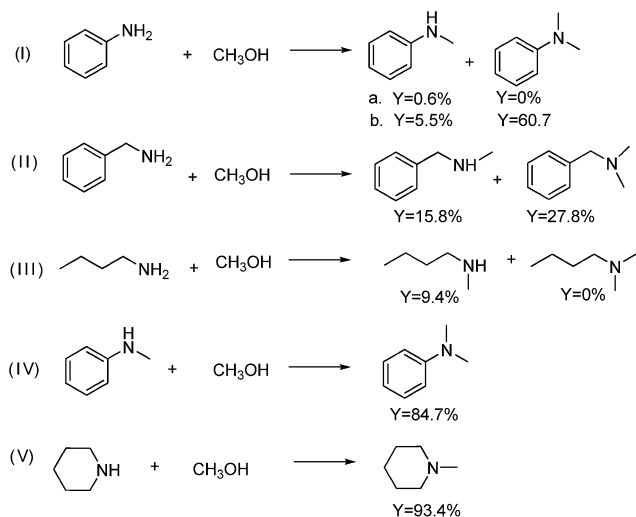
Results and discussion

The Pd/TiO₂ catalysts used in this work were prepared with deposition-precipitation method and followed by reduction

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Scheme 1 Former reports about light promoted *N,N*-dimethylation of amines with methanol (I(a)–V: ref. 35. I(b): ref. 38).

with NaBH_4 solution. The Pd/TiO_2 catalysts with different Pd loadings were obtained after separating, washing and drying. The Pd loading were 0.1%, 0.3%, 0.5%, 0.8% and 1.0%, respectively, and they were denoted as $\text{Pd}_{0.1}/\text{TiO}_2$, $\text{Pd}_{0.3}/\text{TiO}_2$, $\text{Pd}_{0.5}/\text{TiO}_2$, $\text{Pd}_{0.8}/\text{TiO}_2$ and $\text{Pd}_{1.0}/\text{TiO}_2$. According to the ICP-AES analysis, the Pd loadings of these catalysts were 0.1%, 0.34%, 0.47%, 0.85% and 0.81%, respectively. The results suggested that it is difficult to prepare Pd/TiO_2 with Pd loadings above 1% because only 0.81% Pd was supported onto TiO_2 although the theoretically number was 1%. Furthermore the BET surface area of the typical catalyst, *i.e.* $\text{Pd}_{0.8}/\text{TiO}_2$, is $59 \text{ m}^2 \text{ g}^{-1}$. It is similar to the surface of pure TiO_2 , *i.e.* $35\text{--}65 \text{ m}^2 \text{ g}^{-1}$.

In order to investigate the phase structure and the phase composition of the catalysts, the catalyst samples were characterized by XRD. The XRD diffraction patterns of Pd/TiO_2 catalysts are given in Fig. 1. The peaks marked “A” and “R” correspond to anatase and rutile phases, respectively. Neither

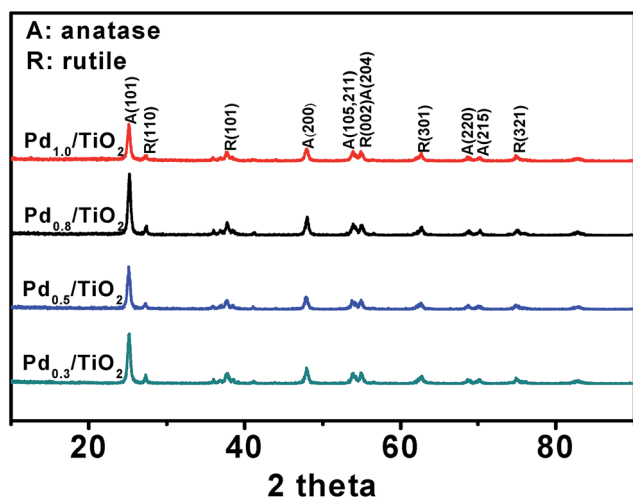


Fig. 1 XRD diffraction patterns of catalysts Pd/TiO_2 .

palladium oxide nor metallic palladium phase was detectable in all the catalysts, which might be attributed to the low Pd loadings and also the good dispersion of nano-Pd particles on the surface of TiO_2 . This was further confirmed by TEM characterization. According to the TEM images shown in Fig. 2, the sizes of the Pd particles determined by the TEM observations were 1.61, 1.86, 1.80 and 1.83 nm, respectively, in catalysts $\text{Pd}_{0.3}/\text{TiO}_2$, $\text{Pd}_{0.5}/\text{TiO}_2$, $\text{Pd}_{0.8}/\text{TiO}_2$ and $\text{Pd}_{1.0}/\text{TiO}_2$. In consideration of the results of XRD and TEM characterizations together, it can be concluded that all the catalysts possess similar structure and the only difference among these samples is the Pd-loading.

As the catalysts were used for light promoted *N,N*-dimethylation of amine or nitro compound, they were further characterized by UV-vis diffuse spectroscopy, Fig. 3. Clearly, the catalysts show increased absorbance at $\lambda > 300 \text{ nm}$ with the increasing of Pd loadings from 0 to 0.8%. It might be attributed to the light scattering caused by the nano-Pd particles.³⁷ However, the intensity of the absorption of $\text{Pd}_{1.0}/\text{TiO}_2$ is weaker

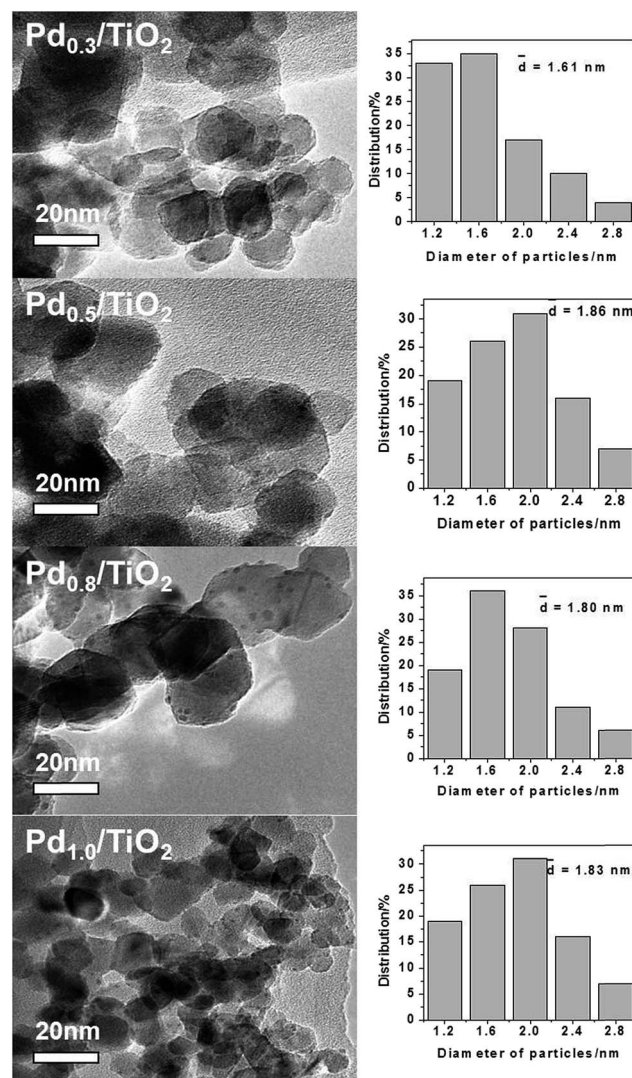


Fig. 2 TEM images and nano-Pd particle size distributions of catalysts Pd/TiO_2 .

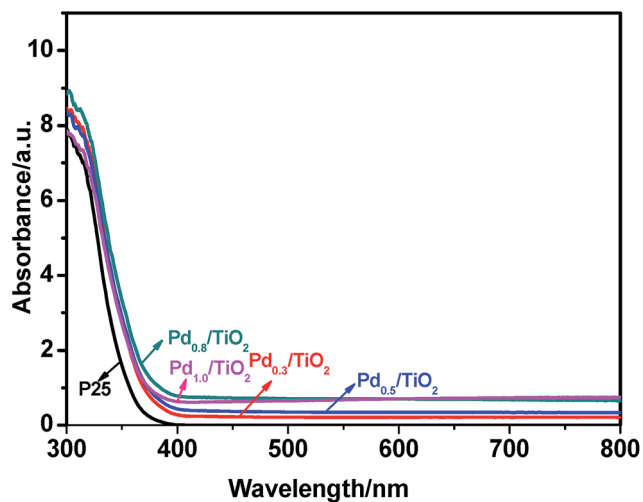


Fig. 3 UV-vis DRS spectra of catalysts Pd/TiO₂.

than Pd_{0.8}/TiO₂, because the real Pd loading of Pd_{1.0}/TiO₂ is 0.81% based on the ICP-AES analysis.

Following, the catalytic performance of the Pd/TiO₂ catalysts were screened and the reaction conditions were optimized with *N,N*-dimethylation of aniline with CH₃OH as a model reaction. The corresponding results were summarized in Table 1. First, TiO₂ without modification by Pd was used as catalyst and no reaction was observed, which was similar to the result under catalyst free condition (entries 1 and 2). Therefore the TiO₂ itself is inactive for the *N*-methylation reaction of amine. Then, the Pd/TiO₂ catalysts with different Pd loadings were screened and we found that the yields of *N,N*-dimethyl aniline increased with the Pd loadings and the highest yield was 81% when using

Table 1 Catalyst screening and reaction conditions optimization using *N,N*-dimethylation of aniline as model reaction^a

Entry ^a	Catalyst	Yield ^b /%
1	TiO ₂	0
2	—	0
3	Pd _{0.1} /TiO ₂	5
4	Pd _{0.3} /TiO ₂	8
5	Pd _{0.5} /TiO ₂	52
6	Pd _{0.8} /TiO ₂	81
7	Pd _{1.0} /TiO ₂	75
8	Pt/TiO ₂	10
9	Au/TiO ₂	3
10	Ru/TiO ₂	0
11 ^c	Pd _{0.8} /TiO ₂	34
12 ^d	Pd _{0.8} /TiO ₂	0

^a Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg), argon, UV (365 nm LED), r.t., 15 h. ^b The yields were obtained by GC-FID using biphenyl as external standard material. ^c The catalyst was prepared according to the ref. 37. ^d Without UV irradiation.

Pd_{0.8}/TiO₂ as catalyst (entries 3–7). Thus the addition of Pd is essential for the *N*-methylation reaction of amine with methanol. In order to explore the catalytic performance of other noble metals such as Pt, Au and Ru, *etc.*, catalysts Pt_{0.8}/TiO₂, Au_{0.8}/TiO₂ and Ru_{0.8}/TiO₂ were also prepared and tested by this reaction but the yields to the desired product were all <10% (entries 8–10). Thus the Pd is vital to gain the high activity in *N*-methylation reaction. The influence of the catalyst preparation method on the catalytic activity was further studied. A Pd/TiO₂ with the same Pd loading was prepared with impregnation–calcination–reduction procedure³⁷ but the yield to the *N,N*-dimethyl aniline was only 34%. Finally, we try to exclude the UV irradiation and perform the reaction under sun light but no any *N*-methylation product was formed. Undoubtedly, the UV irradiation was crucial to realize the room temperature *N,N*-dimethylation of aniline with methanol.

After optimizing the reaction conditions with aniline *N,N*-dimethylation, the present protocol was extended to the *N*-methylation reactions of other amines including secondary amines, aromatic amines and aliphatic amines as well as aromatic nitro compounds. The results of the *N*-methylation of secondary amines were summarized in Table 2. Clearly, cyclic aliphatic secondary amines including morpholine, piperidine, piperazine, and tetrahydropyrrole can be converted into the corresponding *N*-methyl tertiaryamines with 86–96% yields (entries 1–6) and the heterocycles containing N and O atoms didn't retard the catalytic activity. Except for cyclic aliphatic secondary amines, the reaction was also successful for the

Table 2 *N*-methylation of aliphatic secondary amines with methanol^a

Entry	Substrates	Products	Yields ^b (%)
1			89
2			96
3			90
4			95
5			87
6			86
7			93 ^c

^a Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg, Pd_{0.8}/TiO₂), argon, UV (365 nm LED), r.t., 10–15 h. ^b The yields were obtained by GC-FID using biphenyl as standard material. ^c Isolated yield.

Table 3 *N,N*-dimethylation of primary amines with methanol^a

$\text{R-NH}_2 \text{ or } \text{R-CH}_2\text{NH}_2 \xrightarrow[\text{Pd/TiO}_2]{\text{CH}_3\text{OH, hv}} \text{R-N(CH}_3)_2 \text{ or } \text{R-CH}_2\text{N(CH}_3)_2$			
Entry	Substrates	Products	Yields ^b (%)
1			81
2			71
3			87
4			96
5			83
6			97
7			94
8			89
9			80
10			81
11			90
12			97
13			97 ^c
14			96
15			98 ^c
16			74(69 ^c)

^a Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg, Pd_{0.8}/TiO₂), argon, UV (365 nm LED), r.t., 10–15 h. ^b The yields were obtained by GC-FID using biphenyl as standard material. ^c Isolated yield.

N-methylation of dicyclohexylamine. The yield to the desired product was 93% (entry 7).

Then, aromatic primary amines with different substituents on their phenyl rings were examined (Table 3). Various structurally diverse anilines, regardless of the presence of electron-withdrawing or donating functional groups or no group, could be *N,N*-dimethylated with CH₃OH to give the corresponding tertiary amines in excellent yields (71–96%, entries 1–5). Next, the *N,N*-dimethylation reactions of anilines with two groups were investigated under the same reaction conditions. To our delight, the desired products were also obtained in good to high yields, *i.e.* 94% and 97% (entries 6 and 7). Thus, the position of the substituent does not significantly affect the reactivity of aniline derivatives. Furthermore, we studied the *N*-methylation reaction of benzylamine and *N,N*-dimethylbenzylamine was produced with 89% yield (entry 8). Benzylamines with different substituents such as methyl, methoxy and α -methyl groups were transformed into the corresponding *N*-methyl tertiary amines with 80–90% yields (entries 9–11). The scope and limitations of this practical methodology were examined in some aliphatic primary amines involving cyclohexylamine and dodecanamine and different diamines. Good to excellent yields, *i.e.* 74–98%, were generally gained (entries 12–16).

Given that the *N*-methylation and *N,N*-dimethylation of amines proceeded smoothly, the catalytic activity of Pd_{0.8}/TiO₂ in the reductive *N,N*-dimethylation of nitro compounds was further explored. In this transformation, except for behaving as the methyl source for *N*-methylation reaction, methanol is also

Table 4 Reductive *N,N*-dimethylation of nitrobenzene with methanol^a

$\text{R-NO}_2 \xrightarrow[\text{Pd/TiO}_2]{\text{CH}_3\text{OH, hv}} \text{R-N(CH}_3)_2$			
Entry	Substrates	Products	Yield ^b (%)
1			76
2			56
3			53
4			95
5			85

^a Reaction condition: nitro compound (0.2 mmol), methanol (5 mL), catalyst (20 mg, Pd_{0.8}/TiO₂), argon, UV (365 nm LED), r.t., 15–20 h. ^b The yields were obtained by GC-FID using biphenyl as standard material.

Table 5 *N,N*-dimethylation of *p*-Cl-aniline^a

Entry	Catalyst	Yield% of a ^b	Yield of b ^b
1	Pd _{0.8} /TiO ₂	41	56
2	Pd _{0.1} /TiO ₂	71	28
3	Pd _{0.3} /TiO ₂	90	8
4	Pd _{0.5} /TiO ₂	47	50

^a Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg), argon, UV (365 nm LED), r.t., 5 h. ^b The yields were obtained by GC-FID using biphenyl as standard material.

the hydrogen donor for the reduction of nitro compounds to aniline derivatives (Table 4). Indeed, *N,N*-dimethylaniline was formed in 76% yield when nitrobenzene was subjected to our catalytic system (entry 1). Under the same reaction conditions, a range of aromatic nitro compounds were examined. It was found that *o*-Me and *p*-Me nitrobenzene reacted with methanol to give the desired products in moderate yields, *i.e.* 56% and 53% (entries 2 and 3). In reverse, 1,3-dimethyl-2-nitrobenzene was more active for this transformation and 95% yield to the desired product was obtained (entry 4). In addition, *o*-MeO nitrobenzene was transformed into corresponding *N,N*-dimethyl-*o*-methoxyl aniline with 85% yield (entry 5).

Table 6 Selective methylation of different halogenated aniline^a

Entry	Substrates	Catalyst	Product	Yield ^b (%)
1		Pd _{0.3} /TiO ₂		54
2		Pd _{0.3} /TiO ₂		65
3		Pd _{0.3} /TiO ₂		90
4		Pd _{0.3} /TiO ₂		8
5		Pd _{0.3} /TiO ₂		22

^a Reaction condition: amine (0.2 mmol), methanol (5 mL), catalyst (20 mg), argon, UV (365 nm LED), r.t., 5 h. ^b The yields were obtained by GC-FID using biphenyl as standard material.

N,N-dimethyl anilines containing chlorine group are important chemical intermediates but dechlorination reaction often occurs during *N,N*-methylation especially under UV light irradiation. Therefore we try to see if the *N,N*-dimethylation reaction can progress well with our catalyst system using *p*-Cl-aniline as a model substrate (Table 5). Commonly the dechlorination reaction occurred when the typical catalyst Pd_{0.8}/TiO₂ was employed (entry 1). The yield to the desired product was only 41%. Therefore we try to improve the reaction by applying catalysts with lower Pd loadings, *i.e.* Pd_{0.1}/TiO₂, Pd_{0.3}/TiO₂ and Pd_{0.5}/TiO₂. To our delight the dechlorination reaction can be retarded remarkably if catalyst Pd_{0.3}/TiO₂ was used and the yield to *N,N*-dimethyl-*p*-Cl-aniline reached 90% (entries 2–4). If the Pd loading was too low, for example, if applying Pd_{0.1}/TiO₂ as catalyst, the yield to *N,N*-dimethyl-*p*-Cl-aniline decreased again (entry 2). Possibly the dechlorination reaction turned fast with the presence of less Pd. Then the *N,N*-dimethylation reactions of *o*- and *p*-Cl-aniline were further performed and the yield to the corresponding products were 54% and 65% (Table 6, entries 1–3). For the *N,N*-dimethylation reactions of *m*- and *p*-Br-aniline, the yields to the desired products were only 8% and 22% no matter catalyst Pd_{0.1}/TiO₂ or Pd_{0.3}/TiO₂ was used (entries 4 and 5). It might be attributed to the easily debromination of the reactants under UV irradiation and this Pd/TiO₂ might not be suitable for this transformation.

In order to reveal the reaction mechanism, the reaction of aniline with methanol was traced by GC-MS to check the possible reaction intermediates, and the quantity variations of several typical intermediates were shown in Fig. 4. Almost all the aniline was exhausted at the initial stage of the reaction and the possible product was *N*-methylaniline *via* the reaction of aniline with formaldehyde, which was generated by the deprotonation of methanol on TiO₂. As the amount of *N*-methylaniline and *N*-methyl aniline decreased fast, we assume that the *N*-methylaniline was hydrogenated to *N*-methyl aniline and the *N*-methyl aniline will react with formaldehyde again, and *N,N*-methyl aniline formed after further reduction.

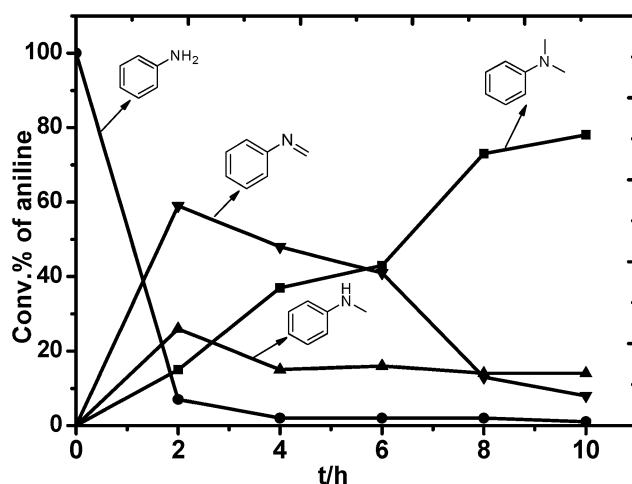


Fig. 4 Time-dependent aniline conversion and products selectivity.

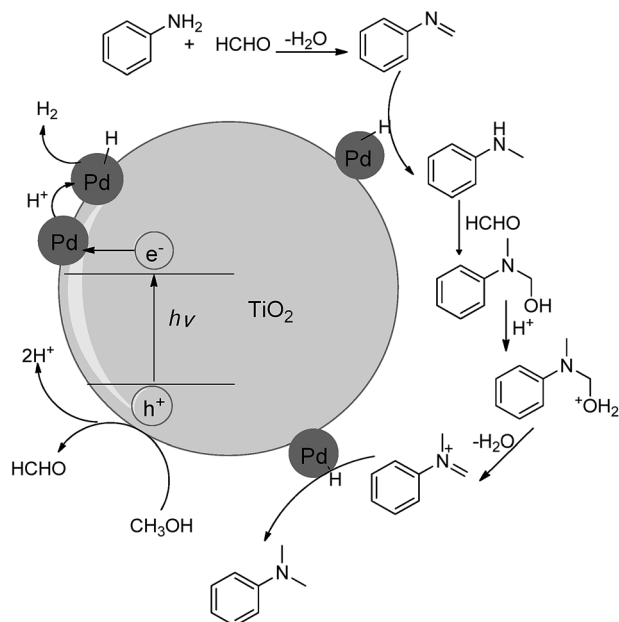


Fig. 5 Proposed reaction mechanism for the light promoted *N,N*-dimethylation of aniline over Pd/TiO₂.

Based on the above observations, a reaction mechanism was proposed and illustrated in Fig. 5. The reaction is initiated by photoexcitation of TiO₂, generating electron (e⁻) and positive hole (h⁺) pairs. The h⁺ oxidizes methanol to formaldehyde and H⁺. H⁺ is reduced on the surface of Pd particles by the e⁻ transferred from the TiO₂ conduction band and produces a hydride on the particles (H-Pd species). The parts of the hydride on the Pd particles are removed by the coalescence as a hydrogen molecule.³⁷ Following, imine is formed from the condensation of formaldehyde and amines by the Lewis acid site on the TiO₂ surface.³⁹ Next, the imine is hydrogenated to form the corresponding *N*-methylaniline by H-Pd species on the surface of TiO₂. Then, *N*-methylaniline was coupled with formaldehyde again, followed by hydrogenation with H-Pd species and *N,N*-dimethylaniline was generated. The product formation enhancement with the immobilization of Pd might be attributed the Pd particles trap e⁻ on the excited TiO₂ and enhance the charge separation between e⁻ and h⁺.^{39,40}

Conclusions

In conclusion, we found that Pd/TiO₂ can be an active catalyst for the UV-light promoted *N,N*-dimethylation of amines and nitro compounds with methanol at room temperature. By applying this simple catalyst system, high yields of *N,N*-dimethyl amines with various structures can be realized. It offers a green and economic method for the synthesis of *N,N*-dimethyl amines.

Experimental

Typical procedure for catalyst preparation⁴³

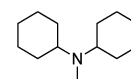
TiO₂ (0.5 g, P25, J&K Scientific, anatase/rutile = 80/20, BET surface, 35–65 m² g⁻¹) was dispersed in deionized water (35 mL)

and H₂PdCl₄ aqueous solution (0.27 mL, 0.25 g/10 mL) were added into the solution under vigorous stirring. The pH value was adjusted to about 10 using 1 M NaOH and the solution was stirred for another 3 h at room temperature. Then NaBH₄ (20 mg) was added to the solution in ice water bath and stirred for 2 h. The solid sample was recovered by centrifugation and washed with water. The obtained solid was dried at 80 °C.

Typical reaction procedure for the *N,N*-dimethylation of amines

Amine (0.2 mmol), catalyst (20 mg) and methanol (99.5% containing 0.05% water, 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 (λ = 365 nm) with magnetic stirring at room temperature for 15 h. Subsequently, 10 mg biphenyl and 5 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

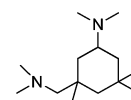
Characterization data of isolated products



N-Cyclohexyl-*N*-methylcyclohexanamine,⁴¹ colorless liquid (93% yield, entry 7, Table 2). The product was separated by vacuum distillation after remove the catalyst by filtration. ¹H NMR (400 MHz, CDCl₃): δ = 1.10–1.24 (m, 2H), 1.27–1.33 (m, 8H), 1.61 (d, 2H), 1.80–1.84 (m, 8H), 2.28 (s, 3H), 2.50–2.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 61.8, 34.6, 32.2, 25.3, 24.9; MS (E.I., 70 eV) *m/z* (rel. int.): 196(3), 195(19), 153(13), 152(100), 124(7), 114(10), 112(3), 96(6), 70(21), 55(9), 42(7).

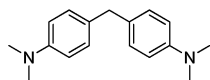


N,N-Dimethyldodecylamine,¹⁵ colorless liquid (97% yield, entry 13, Table 3). The product was separated by vacuum distillation after remove the catalyst by filtration. ¹H NMR (400 MHz, CDCl₃): δ = 0.87 (t, 3H), 1.25–1.29 (m, 20H), 2.27 (t, 2H), 2.22 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 65.6, 52.2, 46.8, 31.9, 30.6, 29.6, 29.3, 27.3, 22.7, 19.2, 14.1, 13.7, 10.2; MS (E.I., 70 eV) *m/z* (rel. int.): 213(6), 212(1), 198(0.5), 184(0.2), 170(0.2), 156(0.2), 142(0.2), 128(0.4), 114(0.6), 100(0.4), 84(1.4), 72(5.2), 69(9.5), 58(100), 59(4.2), 41(4.4), 29(1.8).



3-((Dimethylamino)methyl)-*N,N*,3,5,5-pentamethyl cyclohexanamine, colorless liquid (98% yield, entry 15, Table 3). The product was separated by vacuum distillation after remove the catalyst by filtration. ¹H NMR (400 MHz, CDCl₃): δ = 0.92 (t, 3H), 1.01 (t, 6H), 1.04–1.07 (m, 1H), 1.11–1.14 (m, 1H), 1.45–1.48 (m, 1H), 1.52–1.55 (m, 1H), 1.99 (s, 2H), 2.27 (s, 6H), 2.28 (s, 6H), 2.29 (s, 2H), 2.56–

2.62 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): 74.3, 73.4, 49.2, 47.3, 40.0, 37.8, 35.3, 33.1, 31.9, 27.8, 27.7, 24.1; MS (E.I., 70 eV) m/z (rel. int.): 226 (3), 182 (4), 166 (6), 112 (11), 96 (5), 58 (100), 55 (5), 42 (4); HRMS (ESI) calculated for $\text{C}_{14}\text{H}_{31}\text{N}_2$ [$\text{M} + 1$]: 227.2482, found: 227.2475.



4,4'-Methylenebis(*N,N*-dimethylaniline),⁴² white solid (69% yield, entry 16, Table 3). Mp 86–89 °C. The product was separated by column chromatography (petroleum ether (b.p. 60–90 °C)/EtOAc = 24/1). ^1H NMR (400 MHz, CDCl_3): δ = 2.93 (s, 12H), 3.84 (s, 2H), 6.72 (d, 4H), 7.08 (d, 4H); ^{13}C NMR (100 MHz, CDCl_3): 149.1, 130.4, 129.4, 113.1, 40.9, 39.9; MS (E.I., 70 eV) m/z (rel. int.): 254(100), 253(78), 255(17), 237(15), 210(29), 134(24), 126(17), 118(14).

Catalyst characterization

TEM analysis was carried out with a FEI-TF20 field emission transmission electron microscope. XRD measurements were conducted by an X'Pert PRO (PANalytical) diffractometer. The XRD diffraction patterns were scanned in the 2θ range of 10–90°. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Pd loading was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an Iris advantage Thermo Jarrel Ash device. Diffuse reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (UV-2550 (Shimadzu)) with BaSO_4 as a reference at room temperature.

Acknowledgements

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