Visible-Light-Mediated Photocatalytic Selective N-Methylation of Amines using CO_2 under mild reaction condition via NH_2-MIL-125 (Ti) MOF catalyst

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Abstract

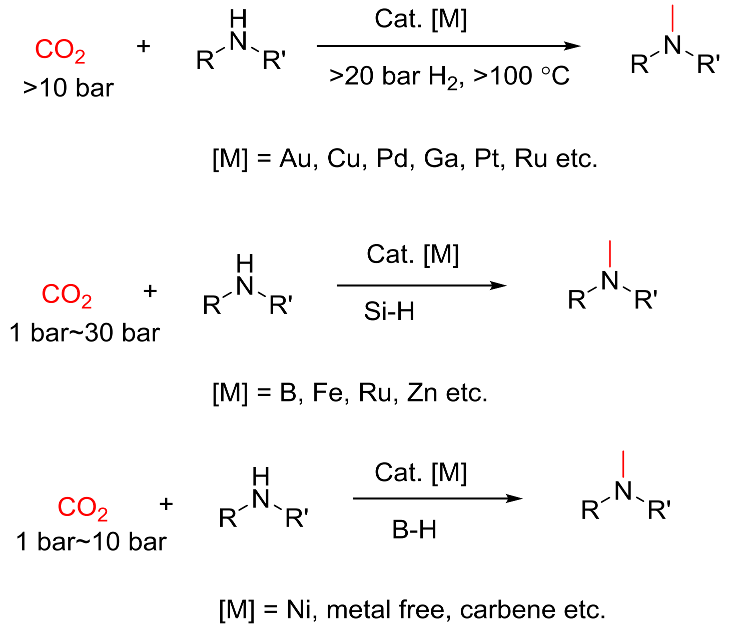
We herein describe a facile synthesis method of novel NH_2-MIL-125 (Ti) metal organic framework as a photocatalyst, and the photochemical system was firstly developed for the direct N-methylation of amines under very mild reaction conditions of one bar CO_2 and $NaBH_4$. According to the optimization of reaction conditions, the selective synthesis of methylamines is achieved in good to excellent conversion and selectivity using visible light mediated photocatalytic system.

Keywords: Photocatalytic; N-Methylation of Amines; CO_2; MOF catalysts

Introduction

In recent decades, carbon dioxide (CO_2) have become a serious threat in environment inspect, which was known as the main factor for the green-house effect. However, conventional methods of the utilization of CO_2, for example, decreasing the CO_2 level in the atmosphere through using chemical synthesis to produce functional chemicals or fuels concurrently.[1] Traditionally, the effective routes to harvest CO_2 is thermal energy activation via using higher reaction temperature or gas pressure, which can make this reaction difficult to industrialize. More attractive and green strategies for the utilization of CO_2 is photocatalytic or electrocatalysis. About the above aspects, photocatalysis is one of the most effective and clean routes, wide application and perspective of pollution degradation and hydrogen evolutions. Remarkable efforts have been directed towards achieving efficient CO_2 activating with photocatalysts by using wide-bandgap semiconductors, such as TiO_2, $SrTiO_3$, ZnO, SiC, ZnS, etc [2, 3]. Besides, the heterogeneous include metal-organic frameworks (MOFs) in addition to the oxide semiconductors such as MIL-101, ZIF-8 and UiO-66 [4, 5] have been recently employed as photocatalysts[6-11], since the modifcation of the coordination chemistry, energy bandgap, organic ligands, and composition of metal clusters can regulate light absorption and charge separation. [12] It is known that MIL(125)-NH_2 (Ti) has a preferable photocatalytic effect upon light excitation, which was consisted of titanium clusters coordinated to the organic linkers, i.e., 2-aminoterephthalic acid. Since previous studies have revealed that the applications of MIL(125)-NH_2 (Ti) in photocatalytic CO_2 reduction, while utilizing CO_2 as a feedstock to produce small molecule chemicals, such as CO, CH_4, HCOOH and CH_3OH.[13-16] However, there is still no report on the CO_2 associated selective photocatalytic N-methylation of amines over MOFs.

As shown in Scheme 1, the reduction approaches of CO_2 have been developed using stable catalysts and renewable reductants (H_2) while requiring hazard conditions with corresponding catalyst.[17, 18] Here, recent advancements on catalytic methylations of amines with CO_2 in presence of mild hydrides such as hydrosilanes or hydroboranes, which feature CO_2 inserted Si-H or B-H bond to form CH_3-B or CH_3-Si species.[19] In the past decade, tremendous progress was made in the synthesis of formamide by using CO_2 as C1 source in the presence of silanes.[20] Meanwhile, related catalytic system can also reduce amides to form amines with hydrosilanes. Therefore, it would be ideal if using CO_2 to synthesis the methylated amines can be realized by means of combining these two processes since it is a more economical one-pot process. Actually, recent studies have revealed that reductive methylation of amines only used one bar of CO_2.[18] However, the mechanism of the N-methylation of amines with CO_2 and hydroboranes is different with hydrosilanes since it is difficult to transform amides to amines by using most hydroboranes, such as BH_3•NH_3 and $NaBH_4$. Taking reductant sodium borohydride ($NaBH_4$) as an example, the N-methylation of amines over all examined CO_2 atmosphere can occur only when heated.[21]Herein, we developed a photocatalysis strategy to realize this process at room temperature with a balloon CO_2.

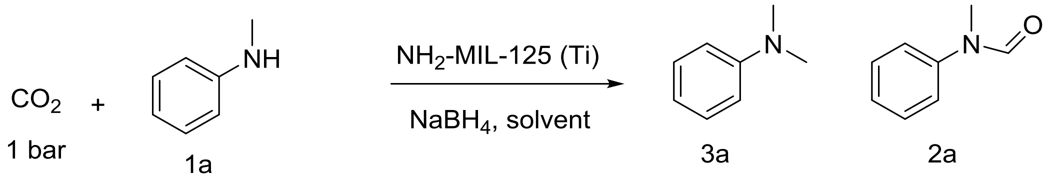


Scheme 1. Catalytic N-methylation of amides.

Result and discussion

To get the optimization of reaction conditions, we used N-methylaniline (1a) as a model substrate to explore photocatalytic selective N-methylation of amines using carbon dioxide (**Table 1**). Rare product can be obtained in the absence of catalyst or in the presence of catalyst but in a dark atmosphere (entry 1, 10, 13). Interestingly, commercial TiO_2 gives a half conversion under the identical conditions (in CH_3CN at 450nm and 12 h, entry 12), which unambiguously indicates that photocatalytic is suitable for for this process but TiO_2 behave as the best catalytic activity in UV region. Besides, trace product is surprisingly detectable in other solvents with commonly used methylation, such as DMF and dioxane (entry 7-8). It is delighted to find that the enough NaBH4 is excellent for high selective formation of N, N-dimethyl aniline (3a) (entry 1, 14). It is noteworthy that the temperature of the reaction system increased on light irradiation because of the photothermal effect.[22] In sharp contrast experiments show that less 3a formation in thermocatalytic system was observed with the 30 % yield of 3a and 10 % yield of 2a at refluxed temperature 80 °C (entry 15), indicating that the N-methylation of amines using carbon dioxide is not driven by heat.

Table 1. Optimization of reaction conditions



Entry	Sol.	NaBH4	t/h	hv/nm & T/°C	Con.(%)	Y (3a) (%)
1	CH_3CN	4 eq	12	450 nm	94	94
2[b]	CH_3CN	4 eq	6	450 nm	64	64
3[c]	CH_3CN	4 eq	24	450 nm	92	92
4	CH_3CN	4 eq	12	520 nm	49	49
5	CH_3CN	4 eq	12	590 nm	40	40
6	CH_3CN	4 eq	12	630 nm	30	30
7	dioxane	4 eq	12	450 nm	trace	trace
8	DMF	4 eq	12	450 nm	18	18
9	CH_3CN	2.5 eq	12	450 nm	64	53
10[d]	CH_3CN	4 eq	12	450 nm	23	23
11[e]	CH_3CN	4 eq	12	450 nm	87	87
12[f]	CH_3CN	4 eq	12	450 nm	51	51
13	CH_3CN	4 eq	12	Dark, rt	20	20
14	CH_3CN	2.5 eq	12	450 nm	64	53
15[g]	CH_3CN	4 eq	12	Dark, 80 °C	40	30
16[h]	CH_3CN	4 eq	12	450 nm	none	none

[a] Reaction conditions: 5 mg of catalyst and 0.3 mmol of 1a in 8 ml of solvent at room temperature for 12 h.
[b] reaction time: 6 h
[c] reaction time:24 h
[d] without catalysis.
[e] 10 mg catalysis.
[f] 5 mg commercial TiO_2
[g] 50 °C
[h] 1 bar N_2

The NH_2-MIL-125 (Ti), obtained by a simple solvothermal reaction, was synthesized following our previous reported procedure.[6] In brief, 2-aminoterephthalic acid (H_2ATA) (2.178 g, 12 mmol), 18 mL of N,N-dimethyformamide (DMF) and 2 mL of MeOH wwere added to a Teflon liner with a magneton, and $Ti(OC_4H_9)_4$ (1 ml, 3 mmol) was added drop by drop. Then, the above mixture was stirred for 30 min, and magneton was removed. Finnally, the whole liner packed stainless steel autoclave and heated at 150 °C for 48 h. The reactor was cooled to room temperature to separate the solid and washed with DMF and methanol, respectively, and the yellow solid was obtained (NH_2-MIL-125 (Ti)).

X-ray diffraction (XRD) patterns indicates that a narrow and sharp diffraction peak indicates that the precursor has a good crystallinity (Figure 1a, black line), which is consistent with the literature.[23] Delightly, XRD characterizations of the reused catalyst still remained same diffraction peak and demonstrated high structural stability (Figure 1a, red line). As expected, the little spectral changes were observed from UV/Vis ab-sorption upon fresh and recycled catalyst (Figure 1b). As shown in Figure 1b, a significant absorption was observed in the wavelength band of 400-500 nm, that is why the catalyst in 450 nm light exhibit the best catalytic effect.

Meanwhile, Transmission electron microscopy (TEM) observation for NH_2-MIL-125 (Ti) as a representative suggests that it has a good crystal structure and rule shape (Figure 2b). Therefore, this is further approved by scanning electron microscope (SEM) (Figure 2a). The elemental energy dispersive X-ray (EDX) mapping indicates uniform distribution of various elements (Figure 2c).

With the optimized reaction conditions in hand, we evaluated a range of substrates for N-methylation of amines with CO_2. As we know, for the amines, we studied fatty amines and aromatic amines with various substituents, including electron withdrawing group and electron donating group, which react with CO_2 to give the corresponding desired methylamine in excellent yields (Table 2). For instance, methyl substituted anilines, including para-, ortho-, meta-, all were obtained in excellent conversion above 80 % and good selectivity above 95 % (Table 2, entry 3-5). Aromatic amines with electron-withdrawing groups such as ;N-methyl-4-fluoroaniline was well tolerated , giving N,N-Dimethyl-4-fluorobenzeneamine conversion of up to 75% without by-product(Table 2, entry 7). Besides, aliphatic amines and large spatial displacement chain aromatic also converted to the corresponding methylamine in high selective conversions (Table 2, entry 9-10).

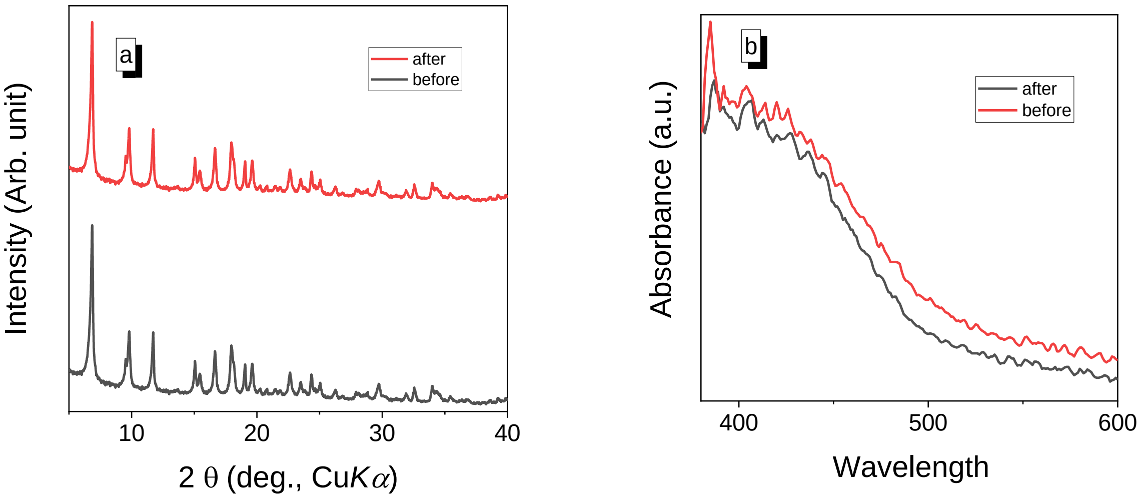


Figure 1. (a) PXRD patterns and (b) UV/Vis absorption of as-synthesized NH_2-MIL-125 before and after reaction of N-methylation of amines.

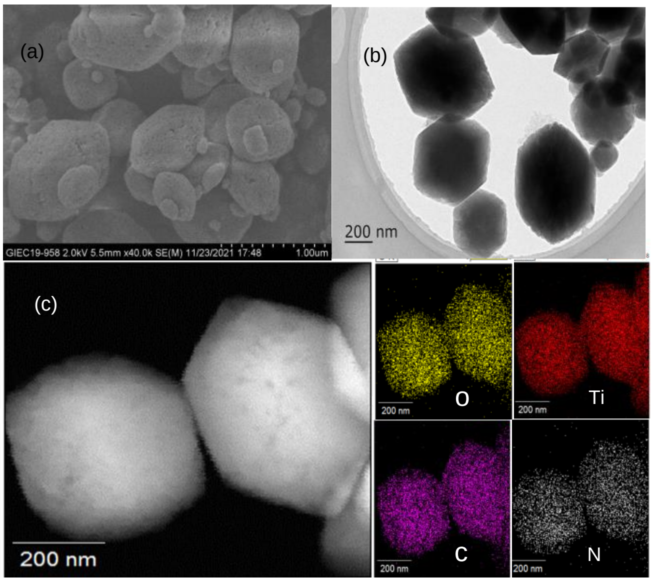
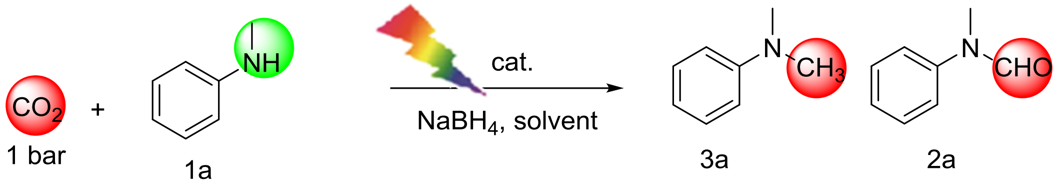
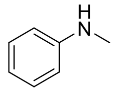
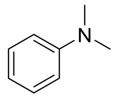
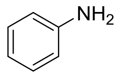
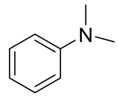
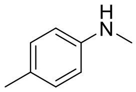
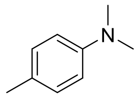
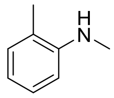
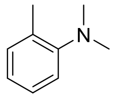
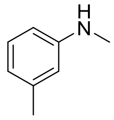
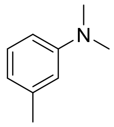
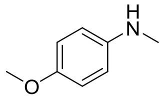
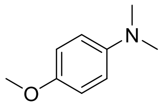
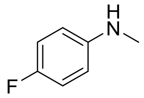
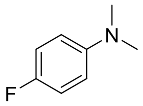
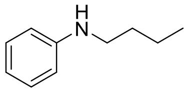
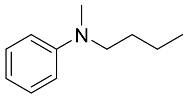
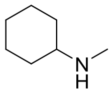
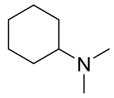


Figure 2. (a)SEM and (b) TEM images of NH_2-MIL-125. (c) High-angle annular dark-field scanning transmission

electron microscopy (HAADF-STEM) image of NH2-MIL-125, and the corresponding O, Ti, C, and Ti elemental mapping.

Table 2. Substrate scope of N-methylation[a].



Entry	Substrate	Product	Con.	Sel.
1			94%	100%
2[b]			>99%	89%
3			>99%	95%
4			80%	100%
5			91%	100%
6			89%	92%
7			75%	100%
9			>99%	100%
10			80%	100%

[a] Reaction conditions: 5 mg of catalyst, 4 eq of $NaBH_4$ and 0.3 mmol of amines in 8 ml of solvent at room temperature for 12 h.

[b] 8 eq of $NaBH_4$

Conclusion

In conclusion, we have firstly developed visible light mediated photocatalytic selective N-methylation of amines with a bar of CO_2 as a sustainable C1 source in presence of $NaBH_4$ as a reductant. According to the optimization of reaction conditions, affording the high selective products of methylamines in excellent yields. MOF as a good crystallinity can maintain shape and structure stable after reaction of N-methylation of amines, which has the potential to be recycled.

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Author contributions J. G. L. and L. L. M supervised and designed the research. X.Z.W wrote the original manuscript. J. G. L reviewed and corrected the manuscript. All authors discussed the results and assisted during manuscript preparation.

Competing interests The authors declare no competing financial interests.

Additional information Correspondence and requests for materials should be addressed to J. G. L. or L. L. M.

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