Visible-Light-Mediated Photocatalytic Selective N-Methylation of Amines using CO$_2$ under mild reaction condition via NH$_2$-MIL-125 (Ti) MOF catalyst

Xiu-Zhi Wei$^{1,3}$, Jianguo Liu$^2$* and Longlong Ma$^{1,2,*}$

$^1$ Department of Engineering Science, University of Science and Technology of China, Hefei 230026, P.R. China.

$^2$ Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China.

$^3$ CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China.

* Corresponding authors e-mail: liujg@seu.edu.cn; mall@seu.edu.cn

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 modification 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$_3$OH.$^{13}$-$^{16}$ 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\textsubscript{2} have been developed using stable catalysts and renewable reductants (H\textsubscript{2}) while requiring hazard conditions with corresponding catalyst.\textsuperscript{17, 18} Here, recent advancements on catalytic methylations of amines with CO\textsubscript{2} in presence of mild hydrides such as hydrosilanes or hydroboranes, which feature CO\textsubscript{2} inserted Si-H or B-H bond to form CH\textsubscript{3}-B or CH\textsubscript{3}-Si species.\textsuperscript{19} In the past decade, tremendous progress was made in the synthesis of formamide by using CO\textsubscript{2} as C1 source in the presence of silanes.\textsuperscript{20} Meanwhile, related catalytic system can also reduce amides to form amines with hydrosilanes. Therefore, it would be ideal if using CO\textsubscript{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\textsubscript{2}.\textsuperscript{18} However, the mechanism of the N-methylation of amines with CO\textsubscript{2} and hydroboranes is different with hydrosilanes since it is difficult to transform amides to amines by using most hydroboranes, such as BH\textsubscript{3}•NH\textsubscript{3} and NaBH\textsubscript{4}. Taking reductant sodium borohydride (NaBH\textsubscript{4}) as an example, the N-methylation of amines over all examined CO\textsubscript{2} atmosphere can occur only when heated.\textsuperscript{21} Herein, we developed a photocatalysis strategy to realize this process at room temperature with a balloon CO\textsubscript{2}.

\[
\begin{align*}
\text{CO}_2 & \quad >10 \text{ bar} \\
& \quad + \quad \begin{array}{c}
\text{H} \\
\text{R} \\
\text{N} \\
\text{R'}
\end{array} \\
& \quad \xrightarrow{\text{Cat. [M]}} \\
& \quad >20 \text{ bar H}_2, >100 ^\circ C \\
& \quad \begin{array}{c}
\text{R} \\
\text{N'} \\
\text{R'}
\end{array}
\end{align*}
\]

[M] = Au, Cu, Pd, Ga, Pt, Ru etc.

\[
\begin{align*}
\text{CO}_2 & \quad 1 \text{ bar} – 30 \text{ bar} \\
& \quad + \quad \begin{array}{c}
\text{H} \\
\text{R} \\
\text{N} \\
\text{R'}
\end{array} \\
& \quad \xrightarrow{\text{Cat. [M]}} \\
& \quad \text{Si-H} \\
& \quad \begin{array}{c}
\text{R} \\
\text{N'} \\
\text{R'}
\end{array}
\end{align*}
\]

[M] = B, Fe, Ru, Zn etc.

\[
\begin{align*}
\text{CO}_2 & \quad 1 \text{ bar} – 10 \text{ bar} \\
& \quad + \quad \begin{array}{c}
\text{H} \\
\text{R} \\
\text{N} \\
\text{R'}
\end{array} \\
& \quad \xrightarrow{\text{Cat. [M]}} \\
& \quad \text{B-H} \\
& \quad \begin{array}{c}
\text{R'} \\
\text{N'} \\
\text{R'}
\end{array}
\end{align*}
\]

[M] = Ni, metal free, carbene etc.

\textbf{Scheme 1}. Catalytic N-methylation of amides.

\textbf{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\textsubscript{2} gives a half conversion under the identical conditions (in CH\textsubscript{3}CN at 450nm and 12 h, entry 12), which unambiguously indicates that photocatalytic is suitable for this process but TiO\textsubscript{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 NaBH\textsubscript{4} 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.\textsuperscript{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 \textdegree 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     | CH₃CN  | 4 eq  | 12  | 450 nm       | 94       | 94         |
| 2ᵇ    | CH₃CN  | 4 eq  | 6   | 450 nm       | 64       | 64         |
| 3ᶜ    | CH₃CN  | 4 eq  | 24  | 450 nm       | 92       | 92         |
| 4     | CH₃CN  | 4 eq  | 12  | 520 nm       | 49       | 49         |
| 5     | CH₃CN  | 4 eq  | 12  | 590 nm       | 40       | 40         |
| 6     | CH₃CN  | 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     | CH₃CN  | 2.5 eq| 12  | 450 nm       | 64       | 53         |
| 10ᵈ   | CH₃CN  | 4 eq  | 12  | 450 nm       | 23       | 23         |
| 11ᵉ   | CH₃CN  | 4 eq  | 12  | 450 nm       | 87       | 87         |
| 12ᶠ   | CH₃CN  | 4 eq  | 12  | 450 nm       | 51       | 51         |
| 13    | CH₃CN  | 4 eq  | 12  | Dark, rt     | 20       | 20         |
| 14    | CH₃CN  | 2.5 eq| 12  | 450 nm       | 64       | 53         |
| 15ᵍ   | CH₃CN  | 4 eq  | 12  | Dark, 80 °C  | 40       | 30         |
| 16ʰ   | CH₃CN  | 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 TiO₂
ᵍ 50 °C
ʰ 1 bar N₂

The NH₂-MIL-125 (Ti), obtained by a simple solvothermal reaction, was synthesized following our previous reported procedure. In brief, 2-aminoterephthalic acid (H₂ATA) (2.178 g, 12 mmol), 18 mL of N,N-dimethyformamide (DMF) and 2 mL of MeOH were added to a Teflon liner with a magneton. Ti(OC₄H₉)₄ (1 ml, 3 mmol) was added drop by drop. Then, the above mixture was stirred for 30 min, and magneton was removed. Finally, 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 (NH₂-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. 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 absorption 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.

| Entry | Substrate | Product | Con. | Sel. |
|-------|-----------|---------|------|------|
| 1     | ![NH2](1a) | ![N](3a) | 94%  | 100% |
| 2<sup>b</sup> | ![NH2](1a) | ![N](3a) | >99% | 89%  |
| 3     | ![H](1a)  | ![N](3a) | >99% | 95%  |
| 4     | ![H](1a)  | ![N](3a) | 80%  | 100% |
| 5     | ![H](1a)  | ![N](3a) | 91%  | 100% |
| 6     | ![O](1a)  | ![N](3a) | 89%  | 92%  |
| 7     | ![F](1a)  | ![N](3a) | 75%  | 100% |
| 9     | ![H](1a)  | ![N](3a) | >99% | 100% |
| 10    | ![H](1a)  | ![N](3a) | 80%  | 100% |

<sup>a</sup> Reaction conditions: 5 mg of catalyst, 4 eq of NaBH<sub>4</sub> and 0.3 mmol of amines in 8 ml of solvent at room temperature for 12 h.

<sup>b</sup> 8 eq of NaBH<sub>4</sub>
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.

Acknowledgment This work was supported financially by the National Key R&D Program of China (2018YFB1501500), National Natural Science Foundation of China (51976225).

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.

Reference
1. McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R., Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework mmen-Mg2(dobpdc). Journal of the American Chemical Society 2012, 134 (16), 7056-7065.
2. Albero, J.; Peng, Y.; García, H., Photocatalytic CO$_2$ Reduction to C2+ Products. ACS Catalysis 2020, 10 (10), 5734-5749.
3. Vu, N.-N.; Kaliaguine, S.; Do, T.-O., Critical Aspects and Recent Advances in Structural Engineering of Photocatalysts for Sunlight-Driven Photocatalytic Reduction of CO$_2$ into Fuels. Advanced Functional Materials 2019, 29 (31), 1901825.
4. Zorainy, M. Y.; Gar Alalm, M.; Kaliaguine, S.; Boffito, D. C., Revisiting the MIL-101 metal–organic framework: design, synthesis, modifications, advances, and recent applications. Journal of Materials Chemistry A 2021, 9 (39), 22159-22217.
5. Rivera-Torrente, M.; Mandemaker, L. D. B.; Filez, M.; Delen, G.; Seoane, B.; Meirer, F.; Weckhuysen, B. M., Spectroscopy, microscopy, diffraction and scattering of archetypal MOFs: formation, metal sites in catalysis and thin films. Chemical Society Reviews 2020, 49 (18), 6694-6732.
6. Sun, D.; Ye, L.; Li, Z., Visible-light-assisted aerobic photocatalytic oxidation of amines to imines over NH2-MIL-125(Ti). Applied Catalysis B: Environmental 2015, 164, 428-432.
7. Fu, Y.; Sun, L.; Yang, H.; Xu, L.; Zhang, F.; Zhu, W., Visible-light-induced aerobic photocatalytic oxidation of aromatic alcohols to aldehydes over Ni-doped NH 2-MIL-125(Ti). Applied Catalysis B: Environmental 2016, 187, 212-217.
8. Xu, J.; Gao, J.; Wang, C.; Yang, Y.; Wang, L., NH2-MIL-125(Ti)/graphitic carbon nitride heterostructure decorated with NiPd co-catalysts for efficient photocatalytic hydrogen production. Applied Catalysis B: Environmental 2017, 219, 101-108.
9. Liu, H.; Zhang, J.; Ao, D., Construction of heterostructured ZnIn2S4@NH2-MIL-125(Ti) nanocomposites for visible-light-driven H2 production. Applied Catalysis B: Environmental 2018, 221, 433-442.
10. Huang, Q.; Hu, Y.; Pei, Y.; Zhang, J.; Fu, M., In situ synthesis of TiO$_2$@NH2-MIL-125 composites for use in
combined adsorption and photocatalytic degradation of formaldehyde. *Applied Catalysis B: Environmental* **2019**, *259*

11. Sun, L.; Yuan, Y.; Wang, F.; Zhao, Y.; Zhan, W.; Han, X., Selective wet-chemical etching to create TiO2@MOF frame heterostructure for efficient photocatalytic hydrogen evolution. *Nano Energy* **2020**, *74*.

12. Yoon, J. W.; Kim, D. H.; Kim, J.-H.; Jang, H. W.; Lee, J.-H., NH2-MIL-125(Ti)/TiO2 nanorod heterojunction photoanodes for efficient photoelectrochemical water splitting. *Applied Catalysis B: Environmental* **2019**, *244*, 511-518.

13. Fu, Y.; Sun, D.; Chen, Y.; Huang, R.; Ding, Z.; Fu, X.; Li, Z., An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-induced activity for CO2 reduction. *Angew Chem Int Ed Engl* **2012**, *51* (14), 3364-7.

14. Cheng, X.-M.; Dao, X.-Y.; Wang, S.-Q.; Zhao, J.; Sun, W.-Y., Enhanced Photocatalytic CO2 Reduction Activity over NH2-MIL-125(Ti) by Facet Regulation. *ACS Catalysis* **2020**, *11* (2), 650-658.

15. Sun, D.; Fu, Y.; Liu, W.; Ye, L.; Wang, D.; Yang, L.; Fu, X.; Li, Z., Studies on Photocatalytic CO2 Reduction over NH2-Uio-66(Zr) and Its Derivatives: Towards a Better Understanding of Photocatalysis on Metal–Organic Frameworks. *Chemistry – A European Journal* **2013**, *19* (42), 14279-14285.

16. Gomes Silva, C.; Luz, I.; Llabrés i Xamena, F. X.; Corma, A.; Garcia, H., Water Stable Zr–Benzenedicarboxylate Metal–Organic Frameworks as Photocatalysts for Hydrogen Generation. *Chemistry – A European Journal* **2010**, *16* (36), 11133-11138.

17. Li, Y.; Cui, X.; Dong, K.; Junge, K.; Beller, M., Utilization of CO2 as a C1 Building Block for Catalytic Methylation Reactions. *ACS Catalysis* **2017**, *7* (2), 1077-1086.

18. Lin, S.; Liu, J.; Ma, L., A review on recent developments in N-methylation using CO2. *Journal of CO2 Utilization* **2021**, *5*4, 101759.

19. Blondiaux, E.; Pouessel, J.; Cantat, T., Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions. *Angewandte Chemie International Edition* **2014**, *53* (45), 12186-12190.

20. Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T., Reductive functionalization of CO2 with amines: an entry to formamide, formamidine and methylamine derivatives. *Green Chemistry* **2015**, *17* (1), 157-168.

21. Zou, Q.; Long, G.; Zhao, T.; Hu, X., Catalyst-free selective N-formylation and N-methylation of amines using CO2 as a sustainable C1 source. *Green Chemistry* **2020**, *22* (4), 1134-1138.

22. Meng, X.; Wang, T.; Liu, L.; Ouyang, S.; Li, P.; Hu, H.; Kako, T.; Iwai, H.; Tanaka, A.; Ye, J., Photothermal Conversion of CO2 into CH4 with H2 over Group VIII Nanocatalysts: An Alternative Approach for Solar Fuel Production. *Angewandte Chemie International Edition* **2014**, *53* (43), 11478-11482.

23. Cheng, X.-M.; Dao, X.-Y.; Wang, S.-Q.; Zhao, J.; Sun, W.-Y., Enhanced Photocatalytic CO2 Reduction Activity over NH2-MIL-125(Ti) by Facet Regulation. *ACS Catalysis* **2021**, *11* (2), 650-658.