

An Amine-Functionalized Titanium Metal–Organic Framework Photocatalyst with Visible-Light-Induced Activity for CO₂ Reduction**

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The capture and efficient use of CO₂ is an important issue because CO₂ released by burning fossil fuels is a primary cause of global warming. One of the best solutions is to convert CO₂ into valuable organic products by means of solar energy. Thus many research efforts have been made to develop efficient heterogeneous photocatalysts for the reduction of CO₂. The examined photocatalysts range from semiconducting materials, such as TiO₂, CdS, ZnGa₂O₄, and Zn₂GeO₄, to metal-incorporated zeolites including Ti-β-zeolite, Ti-MCM-41, Ti-MCM-48, and ZrCu(I)-MCM-41.^[1,2] The fact that the Ti-immobilized zeolites show even much higher efficiency for the reduction of CO₂ over TiO₂ indicates that the incorporation of Ti into porous materials will be a promising strategy, although almost all currently developed photocatalysts are only active in the region of UV light and their efficiency for the reduction of CO₂ is still quite low.

Metal–organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials with an extended 3D network which have shown a variety of potential applications.^[3–9] Especially, MOFs are used for the development of heterogeneous catalysts. In fact, a variety of heterogeneous MOF catalysts has been realized over the past decade by introducing different types of catalytic sites into a porous MOF matrix.^[9] Photocatalysis is a unique kind of heterogeneous catalysis which involves the use of a light source. Theoretically, it is also feasible to develop MOF photocatalysts by immobilizing photoactive catalytic sites in MOF materials. The effective use of solar light can be easily achieved by modifications on the metal ions or the organic ligands in the MOFs.^[10] Although theoretically established, a successful tuning of the absorption of the MOFs for their

application in visible light photocatalysis has not yet been realized experimentally. Besides this matter, only a couple of MOFs have been reported to show photocatalytic activities for dye degradation and water splitting.^[11] Motivated by the above-mentioned discoveries on the Ti-incorporated zeolite photocatalysts, we initiated a research program to develop photoactive MOF photocatalysts for the reduction of CO₂ after a Ti-based MOF Ti₈O₈(OH)₄(bdc)₆ (MIL-125(Ti)) had been reported (BDC = benzene-1,4-dicarboxylate).^[12] This type of MOF material cannot only introduce high density of the immobilized Ti sites within porous MOFs, but it can also lead to isostructural MOFs, the photocatalytic properties of which can simply be tuned by incorporation of BDC derivatives. Indeed, the introduction of NH₂ groups in BDC in the MIL-125(Ti) material to prepare isostructural NH₂-MIL-125(Ti) for H₂ adsorption was recently reported by Zloteeva et al.^[13] Herein we report for the first time a targeted photoactive catalyst Ti₈O₈(OH)₄(bdc-NH₂)₆ (NH₂-MIL-125(Ti)), which reduces CO₂ even under visible light irradiation (BDC-NH₂ = 2-amino-benzene-1,4-dicarboxylate; ATA = 2-aminoterephthalate).

NH₂-MIL-125(Ti) was synthesized using H₂ATA as a linker. The preparation procedure is described in the Supporting Information. The activated sample was prepared by exchanging the guest solvent in the as-synthesized MOF with anhydrous methanol, followed by evacuation at 200 °C. The good agreement between the XRD patterns of MIL-125(Ti) and NH₂-MIL-125(Ti) indicates the formation of the NH₂-MIL-125(Ti) phase. The presence of NH₂ groups in the organic linkers does not influence the structure of MIL-125(Ti) (Figure 1). A schematic drawing of the structure of NH₂-MIL-125(Ti) is shown in Figure S1 in the Supporting

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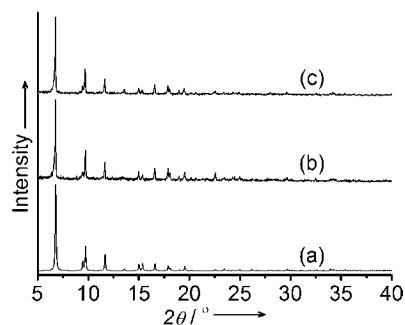


Figure 1. XRD patterns of a) calculated MIL-125(Ti), b) experimental MIL-125(Ti), and c) experimental NH₂-MIL-125(Ti).

Information. Diffuse-reflectance infrared spectroscopy (DRIFTS) analysis of the evacuated sample shows bands corresponding to the symmetric and asymmetric stretching of primary amines (3388 and 3512 cm^{-1} ; Figure S2 in the Supporting Information), confirming that the NH_2 groups are free without coordination. The architectural stability and permanent porosity of $\text{NH}_2\text{-MIL-125(Ti)}$ can be confirmed by the N_2 adsorption/desorption isotherms of the guest-free $\text{NH}_2\text{-MIL-125(Ti)}$. The BET and Langmuir surface area are determined to be 1302 and $1719\text{ m}^2\text{ g}^{-1}$, respectively (Figure S3 in the Supporting Information). The BET specific surface area of the as-prepared $\text{NH}_2\text{-MIL-125(Ti)}$ is slightly higher than that reported previously ($1203\text{ m}^2\text{ g}^{-1}$), but it is lower than the theoretical one determined based on the parent MIL-125(Ti) (close to $2140\text{ m}^2\text{ g}^{-1}$).^[12,13] The lower BET surface area value may be attributed to a partial blocking of the pores by the free ligand as evidenced from thermogravimetric analysis (TGA), IR and Raman spectra (Figure S4–S6 in the Supporting Information). A significant change in $\text{NH}_2\text{-MIL-125(Ti)}$ induced by the amino functionality is its optical absorption. MIL-125(Ti) shows an absorption edge to 350 nm , whereas $\text{NH}_2\text{-MIL-125(Ti)}$ shows an extra absorption band in the visible light region with the absorption edge extending to around 550 nm , in agreement with the bright yellow color (Figure 2 and inset). The

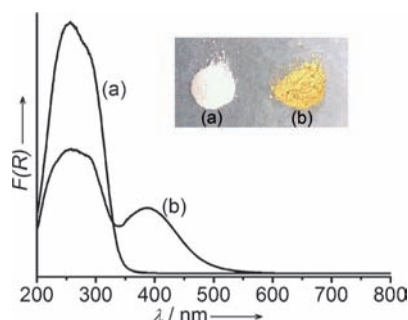


Figure 2. UV/Vis spectra of a) MIL-125(Ti) and b) $\text{NH}_2\text{-MIL-125(Ti)}$. The inset shows the samples.

absorption in $\text{NH}_2\text{-MIL-125(Ti)}$ is induced by O to Ti charge transfer (LMCT = ligand-to-metal charge transfer) in $\text{TiO}_5(\text{OH})$ inorganic clusters. However, the linker ATA influences the charge transfer in these $\text{TiO}_5(\text{OH})$ clusters. The formation of a MOF with absorption in the visible light region by substituting the organic linker H_2BDC by H_2ATA was also observed over a Zr-based MOF $\text{NH}_2\text{-UiO-66}$.^[11c]

Another change in $\text{NH}_2\text{-MIL-125(Ti)}$ induced by the amino functionality is its adsorption capability toward CO_2 . The comparison of CO_2 adsorption isotherms over these two MOFs shows that $\text{NH}_2\text{-MIL-125(Ti)}$ has a higher adsorption capability toward CO_2 than MIL-125(Ti) (Figure 3). At 1 atm and 273 K , the maximum CO_2 uptake for $\text{NH}_2\text{-MIL-125(Ti)}$ is $132.2\text{ cm}^3\text{ g}^{-1}$, whereas the parent MIL-125(Ti) takes up $98.6\text{ cm}^3\text{ g}^{-1}$. The observation of an increase of adsorption capability toward CO_2 over $\text{NH}_2\text{-MIL-125(Ti)}$ as compared to the parent MIL-125(Ti) is within expectation because aromatic molecules functionalized with some polar substituent

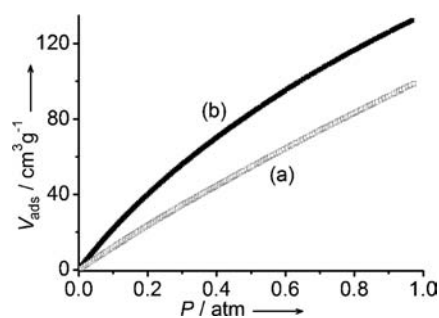


Figure 3. CO_2 adsorption isotherms (1 atm , 273 K) of a) MIL-125(Ti) (\square) and b) $\text{NH}_2\text{-MIL-125(Ti)}$ (\blacksquare).

groups like $-\text{OH}$, $-\text{COOH}$ or $-\text{NH}_2$ enhance the interactions of CO_2 with the functionalized aromatic molecules.^[14] The experimental evidences of the enhancement of CO_2 adsorption over some $-\text{OH}$ or NH_2 -functionalized MOFs have also been well reported in the literature.^[15]

The photocatalytic reduction of CO_2 was performed in acetonitrile (MeCN) with triethanolamine (TEOA) as sacrificial agent under visible light irradiation. $\text{NH}_2\text{-MIL-125(Ti)}$ was pre-treated in vacuum before it was purged with CO_2 . MeCN and TEOA were degassed with CO_2 to remove the dissolved O_2 . The formation of the formate anion HCOO^- in the liquid phase was detected by ion chromatograph (Figure S7 in the Supporting Information). The reaction was shown to be photocatalytic because no HCOO^- was generated in the dark. The inactivity of the parent MIL-125(Ti) under otherwise similar conditions confirms that the visible light photocatalytic activity for CO_2 reduction over $\text{NH}_2\text{-MIL-125(Ti)}$ is actually induced by the amino functionality. A temporal concentration change of HCOO^- with the time of irradiation shows that the amount of HCOO^- formed reached $8.14\text{ }\mu\text{mol}$ in 10 h (Figure 4). XRD, BET, and TGA data, as well as IR and Raman spectra of $\text{NH}_2\text{-MIL-125(Ti)}$ after the photocatalytic reaction showed that $\text{NH}_2\text{-MIL-125(Ti)}$ is stable during the photocatalytic reduction of CO_2 (Figures S8–S12 in the Supporting Information). The comparison of the photocatalytic reduction of CO_2 over $\text{NH}_2\text{-MIL-125(Ti)}$ and the parent MIL-125(Ti) under 365 nm UV irradiation

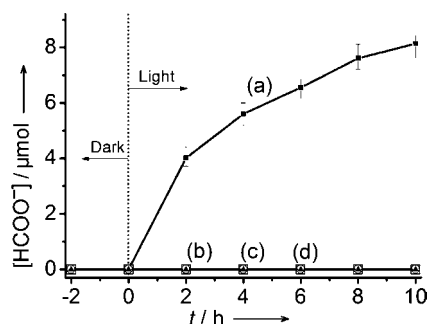


Figure 4. The amount of HCOO^- produced as a function of the time of irradiation over a) $\text{NH}_2\text{-MIL-125(Ti)}$ (\blacksquare), b) MIL-125(Ti) (\square), c) a mixture of TiO_2 and H_2ATA ($19\text{ mg} + 32\text{ mg}$) (\circ), and d) visible light irradiation without a sample (\blacktriangle). The solutions were irradiated using a Xe lamp with filters producing light in the range of $420\text{--}800\text{ nm}$. Photocatalysts: 50 mg , MeCN/TEOA ($5:1$), solution volume: 60 mL .

revealed that $\text{NH}_2\text{-MIL-125(Ti)}$ shows a slightly higher activity, probably because of its higher CO_2 uptake compared to MIL-125(Ti) (Figure S13 in the Supporting Information).

To study the origin of HCOO^- , isotopic $^{13}\text{CO}_2$ was used for the photocatalytic reaction and the obtained product was identified by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the product obtained from the reaction with $^{12}\text{CO}_2$ (Figure S14a in the Supporting Information) shows only peaks corresponding to CD_3CN and TEOA, whereas three additional peaks at 125.8, 159.57, and 165.30 ppm, which can be assigned to dissolved CO_2 , HCO_3^- , and HCOO^- , respectively, were observed for the product obtained from the reaction with $^{13}\text{CO}_2$ (Figure S14b in the Supporting Information). The isotopic $^{13}\text{CO}_2$ reaction confirms that the produced HCOO^- originates from CO_2 .

A recent study by Feng et al. has shown that impurity nanoparticles of ZnO were present in MOF-5.^[16] To exclude the possibility of a minority of N-doped TiO_2 and the production of HCOO^- by the N-doped TiO_2 impurity in the obtained $\text{NH}_2\text{-MIL-125(Ti)}$, UV/Vis diffuse-reflectance spectra (DRS) of the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ and N-doped TiO_2 were compared (Figure S15 in the Supporting Information). A control experiment using N-doped TiO_2 as photocatalyst was also performed (Figure S16 in the Supporting Information). The significant difference in the light absorption profiles of the N-doped TiO_2 and the as-prepared $\text{NH}_2\text{-MIL-125(Ti)}$ implies the absence of N-doped TiO_2 in the product. The control experiment at wavelengths longer than 450 nm shows that 3.83 μmol of HCOO^- was formed over the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ after 10 h of irradiation, whereas no HCOO^- was formed over N-doped TiO_2 because this material does not absorb at wavelengths longer than 450 nm. This result clearly indicates that the photocatalytic reduction of CO_2 to HCOO^- takes place over $\text{NH}_2\text{-MIL-125(Ti)}$.

An interesting photochromic phenomenon was observed over $\text{NH}_2\text{-MIL-125(Ti)}$ during the photocatalytic reaction. When the suspension of $\text{NH}_2\text{-MIL-125(Ti)}$ and TEOA in MeCN was irradiated with visible light in the presence of N_2 , the color of the reaction suspension changed from the original bright yellow to green. However, when CO_2 or O_2 was introduced into the reaction system, the green color of the suspension changed gradually back to the original bright yellow (Figure 5). A color change from white to gray-blue in the presence of alcohols was previously reported for the parent MIL-125(Ti) photocatalyst except that this change

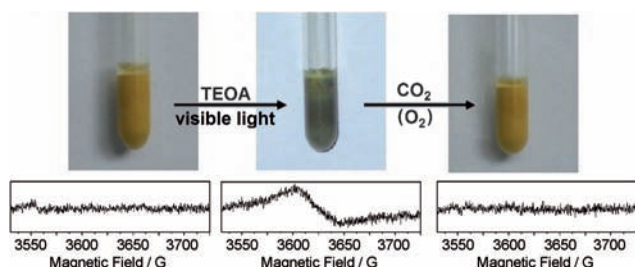
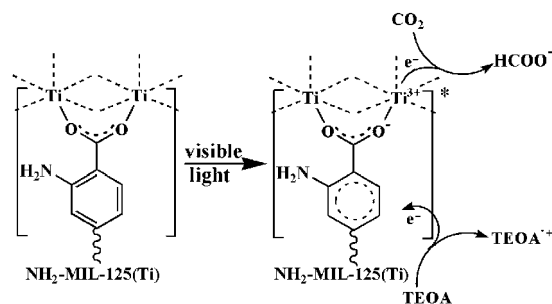


Figure 5. Photos and corresponding ESR spectra of $\text{NH}_2\text{-MIL-125(Ti)}$ under different conditions: a) fresh $\text{NH}_2\text{-MIL-125(Ti)}$, b) TEOA, visible light, and c) after the introduction of CO_2 (or O_2).

occurred upon UV irradiation. The studies on MIL-125(Ti) show that the photochromic phenomenon is ascribed to the presence of the intervalence electron transfer from the optically induced hopping of electrons from Ti(III) to Ti(IV) sites in the titanium oxo-clusters.^[12] In our experiment, the ESR spectrum of the solid with green color shows a broad signal corresponding to Ti^{3+} (Figure S17 in the Supporting Information). The UV/Vis spectrum of the solid with green color also shows intensive absorption in the visible light region, because of $\text{Ti}^{3+}\text{-Ti}^{4+}$ intervalence charge transfer in titanium oxo-clusters (Figure S18 in the Supporting Information).

These experimental observations help to shed some light on the deduction of the mechanism of the reduction of CO_2 over $\text{NH}_2\text{-MIL-125(Ti)}$ (Scheme 1). Upon light absorption in



Scheme 1. Proposed mechanism for the photocatalytic CO_2 reduction over $\text{NH}_2\text{-MIL-125(Ti)}$ under visible light irradiation.

the LMCT band, a long-lived excited charge separation state occurs by transferring an electron from an organic ligand to Ti^{4+} . This process is similar to the generation of electrons and holes over photoexcited metal oxide semiconductors. Ti^{4+} is thus reduced to Ti^{3+} whereas TEOA acts as an electron donor. The existence of Ti^{3+} in the titanium oxo-clusters of $\text{NH}_2\text{-MIL-125(Ti)}$ explains the color change from the bright yellow to green in the presence of N_2 upon visible light irradiation and is confirmed by ESR and UV-DR spectra. When CO_2 is introduced into the suspension, the reduction of CO_2 by Ti^{3+} to HCOO^- occurs. This can explain the observation of a gradual color change of the suspension from green to original bright yellow when CO_2 is introduced to the reaction system. Therefore, a complete photocatalytic cycle can be achieved by reduction of CO_2 to HCOO^- by Ti^{3+} in the presence of TEOA as electron donor. The introduction of O_2 can have a similar effect as CO_2 because O_2 can also be reduced by Ti^{3+} .

When the photocatalytic study was carried out using benzyl alcohol as electron donor upon visible light irradiation, no HCOO^- was detected and the introduction of CO_2 into the reaction system did not change the green color back to yellow, although a similar color change from bright yellow to green was observed. Apparently, in addition to acting as an electron donor, TEOA can facilitate the photocatalytic CO_2 reduction because of its more basic nature. A previous study also showed that the presence of a base in the reaction system supports the hydrogenation of CO_2 to formate.^[17]

In conclusion, the photocatalytic reduction of CO_2 to HCOO^- under visible light irradiation is for the first time realized over a photoactive Ti-containing MOF, $\text{NH}_2\text{-MIL-125(Ti)}$, which is fabricated by a facile substitution of ligands in the UV-responsive MIL-125(Ti) material. This work highlights the potential of MOFs as photocatalysts for the reduction of CO_2 . Although the activity for the reduction of CO_2 over the current $\text{NH}_2\text{-MIL-125(Ti)}$ catalyst is still low, considering the versatile coordination chemistry of the metal cations, the availability of different organic linkers, and the possibility to modulate the composition, structure, and properties of the MOFs, we believe that high-efficient MOF-based photocatalysts for the reduction of CO_2 can be obtained. A limitation in the current photocatalytic system is that TEOA has to be used as the sacrificial electron donor, which is not economic and environmentally friendly. A recent report suggests a solution to this problem by recycling the sacrificial amine by coupling the photochemical reduction of CO_2 to a photochemical water splitting reaction.^[18] Although most of the reported MOFs cannot sustain the water oxidation process, some are fairly stable in water. Thus, the photocatalytic cycle is complete and the MOF-based photocatalysts reduce CO_2 in the presence of a recyclable amine as electron donor under solar irradiation. We believe that the present study will stimulate intensive research in MOF-based photocatalysis and will open new perspectives for the development of photocatalysts for the reduction of CO_2 .

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