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Design of cost-efficient and photocatalytically active Zn-based MOFs decorated with Cu₂O nanoparticles for CO₂ methanation

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Here we show for the first time a MOF that is photocatalytically active for the light-assisted CO₂ methanation at mild conditions (215 °C) without the inclusion of metallic nanoparticles or any sacrificial agent. The presence of Cu₂O nanoparticles causes a 50 % increase in the photocatalytic activity. These results pave the way to developping efficient and cost-effective materials for CO₂ elimination.

The development of technologies that allow the efficient fixation and transformation of CO_2 into valuable chemicals such as CH_3OH, or fuels such as CH_4 will allow to decrease the atmosphere emissions of the main greenhouse gas responsible for global warming.[1] One of the traditional routes for this purpose is the Sabatier reaction, that consists in the CO_2 reduction to CH_4 using molecular H_2. This reaction occurs at high temperatures, typically above 550 °C, and requires the presence of a heterogeneous catalyst. In general, high efficiencies can be achieved employing noble metal nanoparticles (NPs) or clusters as active centres supported in high surface area materials.[1,2] Some cost-effective metals such as Cu, Co or Ni can be employed as active centres for CO_2 methanation, although metal NP sintering commonly occurs at high temperatures (~300 °C) causing catalyst deactivation.[2,3] More recently, the photocatalytic version of the Sabatier reaction is becoming a possible alternative, allowing to decrease the reaction temperature with a minimum impact on the resulting catalytic activity and partially avoiding catalyst deactivation by metal NPs aggregation.[4]

During the last 30 years, metal-organic frameworks (MOFs), materials constituted by organic ligands coordinated to metal ions or clusters defining a porous and crystalline network,[5] have been employed for the CO_2 fixation and/or valorisation.[6] In addition, MOFs have shown to be excellent catalysts for different reactions,[7] and are even currently used as photocatalysts,[8] for visible light CO_2 reduction by triethanolamine,[9] or for promoting C-C bond formation.[10] In most of the cases, they exhibit an intrinsic photoresponse which can be combined with the presence of metal NPs in the pores in order to promote charge separation favouring the electron transfer to the substrate.[11] However, the use of MOFs to promote the Sabatier reaction is almost unexplored,[12,13] possibly due to the severe conditions of this reaction that are not compatible with the stability of many MOFs.

In this work, we report the photoassisted CO_2 methanation by a MOF of formula $[Zn_3(btca)_2(OH)_2]$ (H_2btca = 1,2,3-benzotriazole-5-carboxylic acid).[14] This MOF, denoted as **MOF(Zn)-1**, is based on infinite rod-shape secondary building units (SBUs) formed by two independent 6-coordinated Zn(II) centres bridged by hydroxyl groups and by carboxylate and triazolate groups from the ligand (Fig. 1a). This flexible MOF contains 1D pores whose size depends on the degree of solvation (see ESI, Fig. S1 and S2). The CO_2 sorption capacity of **MOF(Zn)-1** has been previously described with different values depending on the activation temperature: Xiao *et al.*[14] reported a BET surface area of 700 m²/g calculated from CO_2 sorption at 1 bar and 195 K when activating the material at 440 °C, whereas Yue *et al.*[15] reported a BET value of 300 m²/g, under the same conditions, when the material was activated at 150 °C. In order to further understand these contradictory results, we have performed a detailed structural analysis on the different degree of breathing depending on the temperature of activation. We concluded that increasing the temperature causes a continuous breathing with a decrease in the volume cell similarly to other reported MOFs (see Fig. S1).[16] However, upon further heating (above 400 °C), the MOF exhibits an irreversible phase transition with an unexpected pore opening and modification of the SBU and metal coordination environment, which is accompanied with some loss of crystallinity (see Fig. S2-S3). The activated sample at 400 °C is referred as **MOF(Zn)-2**.

MOF(Zn)-1 combines the presence of the active counterparts of the benchmark reference material for CO_2 methanation (ZnO), together with a N-electron rich heteroatom network of a porous structure with specific pore

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size for CO_2 interaction. Thus, we have explored the activity of this material for the photoassisted CO_2 methanation by molecular hydrogen, and compared it with **MOF(Zn)-2** and two reference materials, MOF-74(Zn),[17] and MIL-125(Ti)-NH₂.[18] MOF-74(Zn) is very similar to **MOF(Zn)-1** from a structural point of view, as both MOFs are formed by rod-like SBUs of the same metal (Zn^{II}), albeit in the case of MOF-74(Zn) with no nitrogenated ligands (Fig. 1b). MIL-125(Ti)-NH₂ exhibits a structure based on octameric $Ti_8O_4(OH)_4$ oxoclusters and 2-amino-terephtalate dianions, and has been shown to be an efficient photocatalyst.[19]
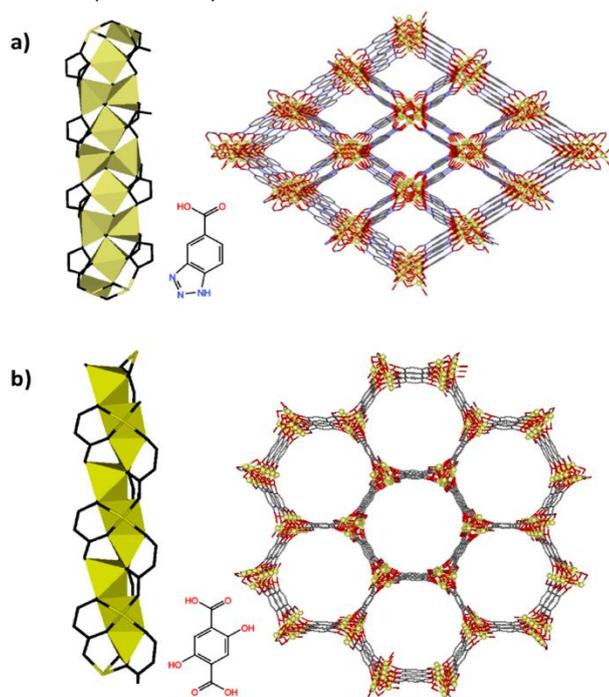

Fig. 1. Representation of crystal structures along *c*-axes of (a) **MOF(Zn)-1** and (b) MOF-74(Zn). The rod-like SBU is shown for each MOF, together with a schematic representation of the ligand.

MOF(Zn)-1 exhibits intrinsic activity for the selective photocatalytic CO_2 methanation under stoichiometric amount of hydrogen at 215 °C under UV-Vis irradiation (Fig. 2). The only product observed is methane, with an initial CH_4 production of 4 μmol·g_{cat}^{-1}·h⁻¹, and 30 μmol·g_{cat}^{-1} after 24 hours. Although this activity value is not large, this is the first time that a bare MOF, i.e. without the addition of any nanoparticle or any sacrificial agent, exhibits photocatalytic activity for the Sabatier reaction. The temporal profile of CO_2 generation exhibits two regimes with two different reaction rates, which has been previously attributed to the effect of H_2O formed in the reaction simultaneously with CH_4 deactivating the catalyst.[4c] Blank control experiments in the presence of the **MOF(Zn)-1** catalyst and H_2 as reducing agent but in the absence of CO_2, do not show the formation of methane. Similarly, performing the photocatalytic reaction at room temperature, or upon irradiation of visible light only, does not produce any methane. Other blank control in the absence of UV-Vis light irradiation results in a methane production lower than 0.1 μmol·g_{cat}^{-1} after 24 h. Importantly,

the catalytic activity of MOF-74(Zn) or MIL-125(Ti)-NH₂ is negligible under the same reaction conditions (see Fig. 2). This lack of photocatalytic activity can be a consequence of the low harnessing ability of these MOFs in comparison to **MOF(Zn)-1,** as their CO_2 adsorption capacity is higher. Interestingly, **MOF(Zn)-2**, which has a wider pore aperture than **MOF(Zn)-1**, is less active (initial production of 2.88 μmol·g_{cat}^{-1}·h⁻¹ and 15 μmol·g_{cat}^{-1} after 24 hours) for the photocatalytic CO_2 methanation than **MOF(Zn)-1**, which can be explained by the modification of the SBU and the loss in crystallinity of the bulk material upon temperature treatment, as shown by X-ray powder diffraction (see Fig. S2).
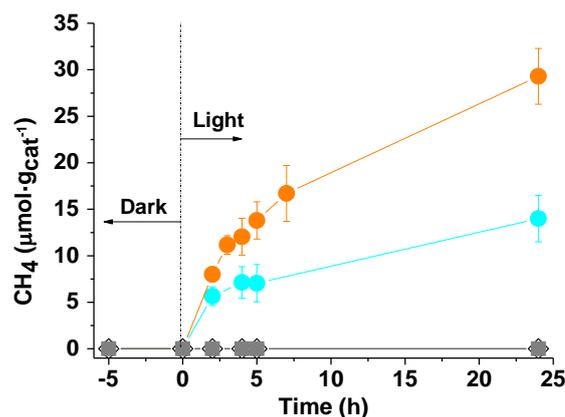

Fig. 2. CH_4 production obtained at 215 °C upon 2236 W·m⁻² irradiation using a 300 W Xe lamp. P_{H2} = 1.05 bar, P_{CO2} = 0.25 bar. **MOF(Zn)-1** (●), **MOF(Zn)-2** (●), MOF-74(Zn) (■),MIL-125(Ti)-NH₂ (◊).

In order to enhance the catalytic activity of **MOF(Zn)-1**, we have evaluated the influence of metal NPs in the pores of the MOF. Recently, Ni NPs encapsulated into the cavities of MIL-101(Cr) have resulted in a stable catalyst for the CO_2 methanation.[12] However, Cu NPs supported on ZnO finely dispersed in the high surface area Al_2O_3 support is a reference industrial material for CO_2 hydrogenation,[20] and it has been previously shown that Cu_2O is an active semiconductor for the photocatalytic CO_2 methanation.[4b] Based on these precedents, we have prepared Cu_2O NPs deposited into **MOF(Zn)-1** by using the photodeposition method. For comparison, Cu_2O NPs were also deposited into **MOF(Zn)-2**, MOF-74(Zn) and MIL-125(Ti)-NH₂ solids.

Specifically, upon UV-Vis irradiation of a MOF suspension in an aqueous Cu^{2+} solution using methanol as sacrificial electron donor, Cu_2O NPs of few nm could be prepared. ICP-OES analyses confirm a ~1 wt% copper loading on the various MOFs. Powder X-ray diffraction (PXRD) measurements of the copper-supported MOFs confirm the stability of the materials during the photodeposition method while no peaks attributable to the diffraction of any copper species could be observed. This failure to detect Cu diffraction peaks can be attributed to the good dispersion of small copper NPs in the MOFs and/or low copper content of the catalysts (1 wt%). In agreement with this hypothesis, TEM analysis reveals that the narrowest copper particle size distribution is achieved using

MOF(Zn)-1 support (1.61±0.46 nm), followed by MIL-125(Ti)-NH$_2$ (4.29±0.95 nm), **MOF(Zn)-2** (5.35±2.36 nm) and MOF-74(Zn) (6.07±1.52 nm) (Fig. S4-S6). The small copper particle size achieved in the Cu$_2$O@**MOF(Zn)-1** is compatible with the internal location inside the pores. SEM measurements show that the morphology of **MOF(Zn)-1** or **MOF(Zn)-2** are not modified after copper deposition (Fig. S7) and copper NPs are well-dispersed in the MOFs (Fig. S8-S9).

XPS spectra of Cu$_2$O@**MOF(Zn)-1** and Cu$_2$O@**MOF(Zn)-2** reveal the presence of the different elements (C, O, N, Zn and Cu) in the samples (Fig. S9-S11). Regarding the high resolution XPS spectrum of Cu2p peak (Fig. S9d), the presence of Cu2p$_{3/2}$ and Cu2p$_{1/2}$ and their deconvolution allows to detect reduced copper species (Cu^0 and/or Cu$^+$) together with Cu^{2+}. It should be noted, however, that under the photocatalytic reaction conditions at 215 °C under H$_2$ flow, the Cu^{2+} would be probably reduced to Cu$^+$,[21] while the reduction of Cu$_2$O to metallic copper starts to take place at temperatures above 300 °C.

The copper-containing MOF samples were evaluated as photocatalysts in the same conditions as pristine MOFs lacking Cu$_2$O nanoparticles (*vide supra*). The temporal evolution of CH$_4$ formation is presented in Fig. 3, which shows, as expected, an enhanced activity upon Cu$_2$O incorporation. As in the case of **MOF(Zn)-1**, the photocatalytic activity of Cu$_2$O@**MOF(Zn)-1** derives exclusively from the UV region. The deposition of copper NPs in MOF-74(Zn) and MIL-125(Ti)-NH$_2$ results in the formation of solids capable of promoting the CO$_2$ photoreduction by H$_2$ to CH$_4$, although it can be clearly observed that the best performing MOF photocatalyst is Cu$_2$O@**MOF(Zn)-1** (initial CH$_4$ production of 10 μmol·g$_{cat}^{-1}$·h^{-1} and 45 μmol·g$_{cat}^{-1}$ after 24 hours), which increased around 50% its photocatalytic activity compared with the pristine MOF lacking Cu$_2$O particles. The estimated TOF of Cu$_2$O@**MOF(Zn)-1**, measured at 2 h after subtracting the activity of **MOF(Zn)-1**, is as high as about 50·10^{-3} s^{-1} at 215 °C, which is much better than reported for Ni@MIL-101(Cr) (1.63·10^{-3} s^{-1} at 300 °C).[12]

To confirm the origin of methane, an additional experiment using ^{13}C^{18}O$_2$ as reagent was performed and the photoproduct analysed by GC-MS (Fig. S15), observing the formation of ^{13}CH$_4$ (m/z 17) and H$_2$^{18}O (m/z 20), accompanied by H$_2$^{16}O (m/z 18), thus corroborating the simultaneous formation of CH$_4$ and H$_2$O.

The PXRD patterns of the used samples show that the MOF materials employed in this study retain their initial crystallinity under the present reaction conditions (Fig. S12). For the most active sample, Cu$_2$O@**MOF(Zn)-1**, TEM measurements of the used sample (Fig. S13) show that the average copper particle size distribution and standard deviation remain constant (1.7 ± 0.9 nm) respect to the fresh sample (1.6 ± 0.5 nm), and ICP-OES analysis of the used sample reveals that the copper content is practically the same than the fresh sample.

In fact, although Cu$_2$O exhibits intrinsic photocatalytic activity in the absence of support, the main limitation of this semiconductor is the stability under photocatalytic conditions,[22] which is enhanced upon incorporation into the pores of **MOF(Zn)-1**, as previously demonstrated.[23]
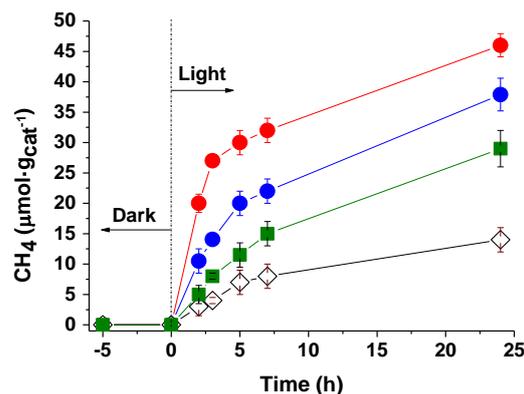

Fig. 3. CH$_4$ production using Cu$_2$O@MOFs working 215 °C upon 2236 W m^{-2} irradiation using a 300 W Xe lamp. P$_{H2}$ = 1.05 bar, P$_{CO2}$ = 0.25 bar. Legend Cu$_2$O@**MOF(Zn)-1** (●), Cu$_2$O@**MOF(Zn)-2** (●), Cu$_2$O@MOF-74(Zn) (■), and Cu$_2$O@MIL-125(Ti)-NH$_2$ (◊).
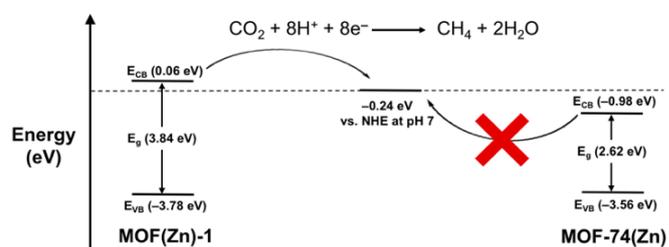

Fig. 4. Energetic diagram for **MOF(Zn)-1** and MOF-74(Zn). E$_g$ has been calculated from the TAUC plot; E$_{VB}$ calculated from the oxidation potential; and E$_{CB}$ has been calculated from the following equation: E$_{CB}$ = E$_g$ + E$_{VB}$ (see Fig. S16-S17 for details).

The higher activity of Cu$_2$O@**MOF(Zn)-1** is attributed to the intrinsic photoactivity of the material. This is revealed by self-activity of the support and, more importantly, further combination with small Cu$_2$O NPs behaving both as semiconductor and co-catalyst close to the Zn-O reduction centres. In addition, we have examined if the presence of incorporated Cu$_2$O NPs increase the charge separation efficiency. The lack of significant changes in the photoluminescence of **MOF(Zn)-1** in the absence and in the presence of occluded Cu$_2$O NPs suggests that there is no charge transfer between the two components, indicating that the charge recombination in **MOF(Zn)-1** is not altered by the presence of Cu$_2$O. The differences in photoactivity between **MOF(Zn)-1** and MOF-74(Zn) is further explained by the energy of the conduction of valence band, which has been experimentally determined by combination of electrochemistry (Fig. S16) and optical spectroscopy (Fig.S17). As can be seen in Fig. 4, the valence band energies are similar in both materials, but the optical band gaps (calculated from the absorption spectra) are remarkably different resulting in a different energy for the conduction bands (0.06 eV vs. −0.975 eV for **MOF(Zn)-1** and MOF-74(Zn) respectively). In fact, in the case of MOF-74(Zn), the conduction band energy is not enough to promote the photochemical reduction of CO$_2$ (−0.24 eV).[24] However, this process is thermodynamically possible in the case of **MOF(Zn)-1**, explaining why this material has intrinsic photocatalytic activity.

Conflicts of interest

There are no conflicts to declare.

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