SUPPORTING INFORMATION

Active site imprinting on Ti oxocluster metal-organic framework

for the photocatalytic hydrogen release from formic acid

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Synthesis of MIP-177-LT.

The synthesis of the Ti-based MOF was performed following the procedure developed by Wang *et al.* [1]. In a typical experiment 200 mg of 3,3',5,5' -tetracarboxydiphenylmethane (H_4mdip) were added to a 25 mL round bottom flask and suspended in 10 mL of formic acid (FA). The suspension was vigorously stirred at room temperature. Afterwards, 400 μL of titanium isopropoxide (Ti(*i*PrO)$_4$) were added dropwise to avoid the formation of white aggregates of precipitate. The reaction mixture was heated under reflux for 48 h. Finally, the obtained product was filtered and the white powder was thoroughly washed with ethanol.

Preparation of MIP-177-LT-AT.

Partly removal of formate groups was performed by an acid treatment of the MOF. In a typical preparation, 1.5 g of MIP-177-LT were suspended in 100 mL of a 1M HCl water solution. The suspension was stirred at room temperature for 24 h [2]. After this period of time, the product was washed with fresh water several times to remove the excess of acid and finally exchanged with acetone. The final product was dried in a vacuum oven.

Powder X-ray Diffraction (PXRD)

PXRD data were collected using a high-throughput Bruker D8 Advance diffractometer working on transmission mode and fitted with a focusing Göbel mirror. The X-ray source was Cu-Kα radiation (λ = 1.5418 Å).

Sorption measurements

Nitrogen sorption data at 77K was collected on a Micromeritics Tristar instrument equipped with LN2 batch. The CO_2, N2 isotherms at 298K were recorded on a Micromeritics Triflex instrument equiped with an ISO cooler to maintain the sample temperature over the measurement. In all the cases the measurements were recorded using ultra-high purity gases (≥4.8 grade). Prior to the adsorption measurement, the sample was degassed under vacuum (10^{-5} mbar) at 200°C over night using a Micromeritics SmartVacPrep degas unit.

NMR analysis

The content of formate species in sample MIP-177-LT_AT was analyzed by liquid proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. The digestion of the sample was performed using a concentrated KOH/D_2O solution. For this, between 10 and 15 mg of sample were dispersed in 600 μL the basic solution. The sample was left stirring overnight. After 12 h, the supernatant was recovered by centrifugation and used for the ^{1}H-NMR analysis, while the remaining powder was discarded.

Photocatalytic Test

FA photodecarboxylation was performed in a 51 mL Pyrex photoreactor equipped with a manometer. The photocatalyst, either MIP-177-LT or MIP-177-LT-AT, was dispersed in the reactor containing 15 mL of FA at the required concentration by sonication in an ultrasound bath. The reaction vessel was subsequently purged with an argon flow for at least 15 min. The photoreactor was irradiated with a collimated circular beam of a 300 W arc Xe lamp as a light source. Every 30 min. the reactor head space was analysed using an Agilent 490 MicroGC (TCD

detector), equipped with two channels (Molsieve 5Å column for H_2 detection and a PorePlot Q column for CO_2 and short chain hydrocarbons). For quantification a previous calibration was made employing commercial gas mixtures with different percentages of gaseous species (Fig. S11). TOF values were calculated applying the following formula:

$$TOF = \frac{n_{H2}(t) \times MW}{ac \times m \times t}$$

In which $n_{H2}(t)$ is the number of evolved H_2 molecules at a given reaction time, t is the reaction time in hours, MW is the formula weight, ac is the number of active centres in the formula, m is the photocatalyst mass and t is the irradiation time.

Turnover frequencies (TOFs) were calculated by using a formula weight of 2115.6 and 1845.6 for MIP-177-LT and MIP-177-LT-AT. It was considered that the formula weight contain 12 active centres corresponding to the Ti ions. For the reference photocatalysts appearing in Table 2, the values were 1664 and 1563 for MIL-125(Ti) (ac=8) and UiO-66(Zr) (ac=6), respectively. For TiO_2 the MW was 80 and ac=1.

Photostability tests were performed with the same reactor and irradiation light spreading 10 mg of dry photocatalyst. The gas composition was analysed with the microGC as indicated above. Cut-off filters of 360 and 400 nm were used to irradiate with photons of wavelength longer than the nominal value of the filter.

Photocurrent measurements were carried out by depositing a suspension in acetylacetone of 1 mg of MIP-177-LT, MIL-125(Ti) or UiO-66 on a freshly cleaned FTO electrode on a surface of 1⌀1 cm2. After drying the solvent the electrode was introduced in a single-compartment cell having Pt wire and AgCl/Ag as counter and reference electrode and aqueous 0.1 M Bu4NPF6 as electrolyte. The cell was exhaustively purged with Ar and connected to an Amel potentiost. The polarization bias was -1 V. The cell was illuminated for 10 sec period with the output of a 150 W Xe lamp followed by a 10 sec period in the dark.

Simulation Methods

All DFT computations performed by using the Vienna *Ab-initio* Simulation Package (VASP-5.4.4) [1, 2] and the projector augmented-wave (PAW) method has been adopted to describe the pseudopotential. The electron exchange-correlation functional was treated by the Perdew−Burke−Ernzerhof functional within the generalized gradient approximation (GGA) scheme.[3] The energy cutoff of the plane wave was set to 500 eV with an energy (force) precision of 10^{-5} eV (0.02 eV per Å). The van der Waals interaction was also included by using Grimme's DFT-D3 method.[4] The Brillouin zone was sampled with a 1 × 1× 1 Monkhorst−Pack *k*-points grid for MIP-177(Ti)-LT clusters, and a 3 × 2 × 1 k-points for $TiO_2(110)$ slab which has five layers, and the bottom three layers were fixed during all the calculations. The LOSTER program was used to study the Crystal Orbital Hamilton Populations (COHP) to give a precise description of the interactions between Ti atoms from MIP-177(Ti)-LT and adsorbed intermediates.[5] To evaluate the adsorption strength of intermediates and the catalytic performance of each elementary step, the Gibbs free energy (ΔG) relative to the total free energy was corrected as follows:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T \times \Delta S$$

where ΔE_{DFT}, ΔE_{ZPE}, T and ΔS are the electronic energy from DFT calculation, the zero-point energy, environmental temperature (298.15 K), and the entropy, respectively.

We defined the adsorption energy (E_{ads}) of intermediate species as follows:

$E_{ads} = E_{total} - E_{substrate} - E_{molecule}$

where E_{total} is the total energy of the adsorption system, $E_{substrate}$ is the energy of a clean substrate, and $E_{molecule}$ is the energy of an isolated molecule.

Figure S1. A: Diffuse reflectance UV-Vis spectra (plotted as the Kubelka-Munk function ofthe reflectance, 1/R) recorded for MIP-177-LT (red) and MIP-177-LT-TA (blue). The circle highlights the difference in the absorption onset due to the presence of TiO2 impurities. B: XRD patterns of MIP-177-LT (green) and MIP-177-LT-TA (blue) in comparison with the simulated MIL-177-LT diffractogram (black). C: Isothermal N_2 adsorption at 77 K of MIP-177-LT (black) and MIP-177-LT-TA (blue) corresponding to a specific area of 641 and 560 $m^2 g^{-1}$, respectively. D: Isothermal CO_2 adsorption/desorption at 298 K on MIL-177-LT. E and F: SEM images of MIP-177-LT (E) and MIP-177-LT-TA (F). G and H: Thermogravimetric analysis (TGA) for sample MIP-177-LT under oxygen atmosphere (5°C/min heating rate) for samples MIP-177-LT (G) and MIP-177-LT_AT (H). Data were recorded on a Mettler Toledo TGA/DSC 2, STAR System apparatus.
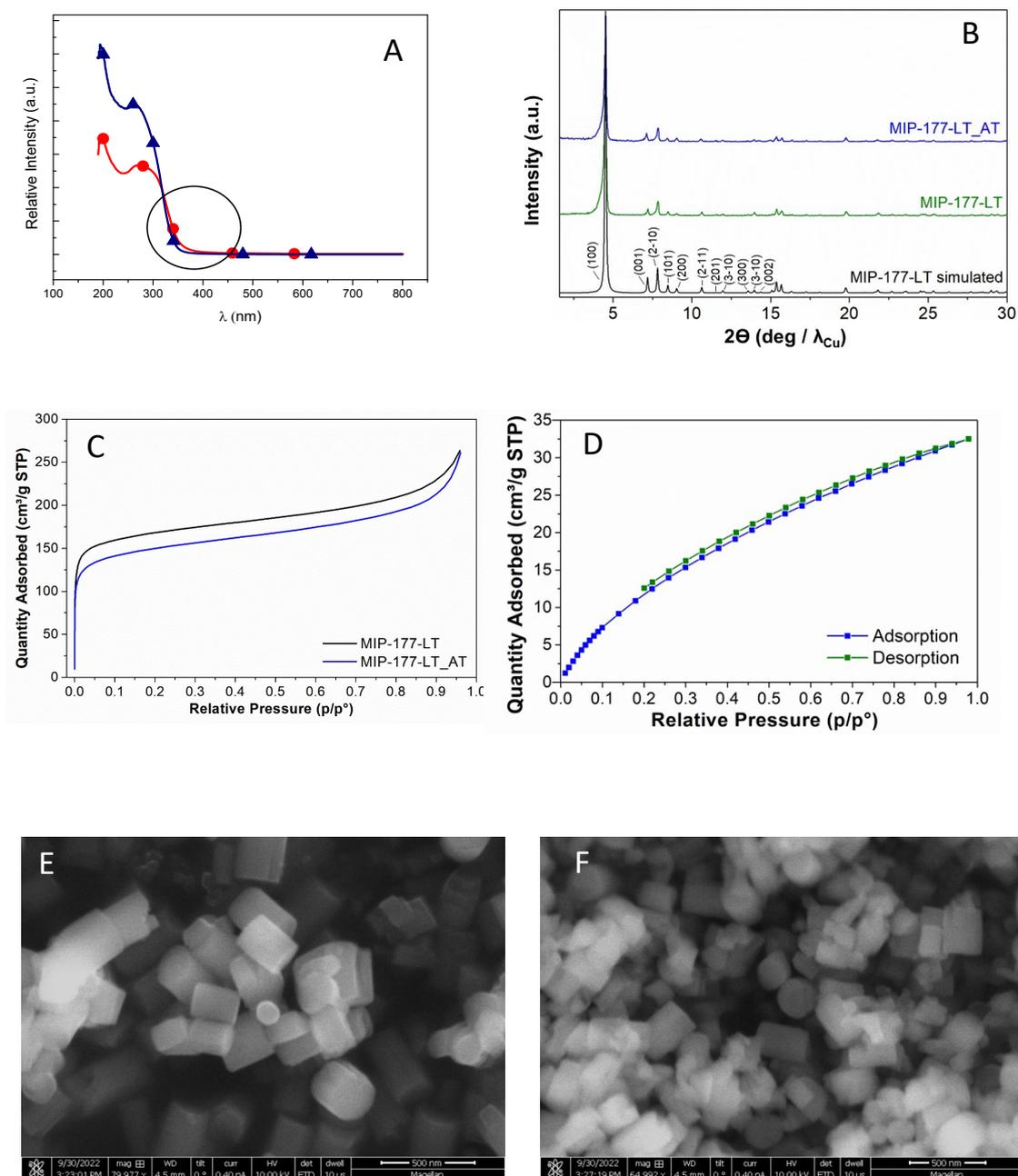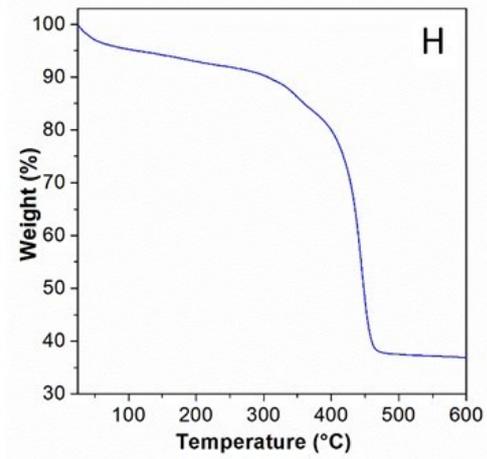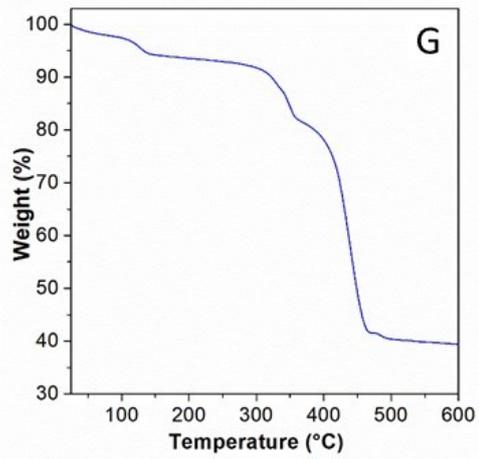
Figure S2. Photograph of the experimental setup used in the photocatalytic H_2 release from FA and the corresponding schematics. (1) 150 W Xe lamp, (2) Fiber optics bringing the beam to the photoreactor vessel, (3) Quartz photoreactor being illuminated from the top by the fiber optics and having a manometer and sampling valve connected to the reactor headspace that can be connected to a micro-GC, (4) magnetic stirrer.
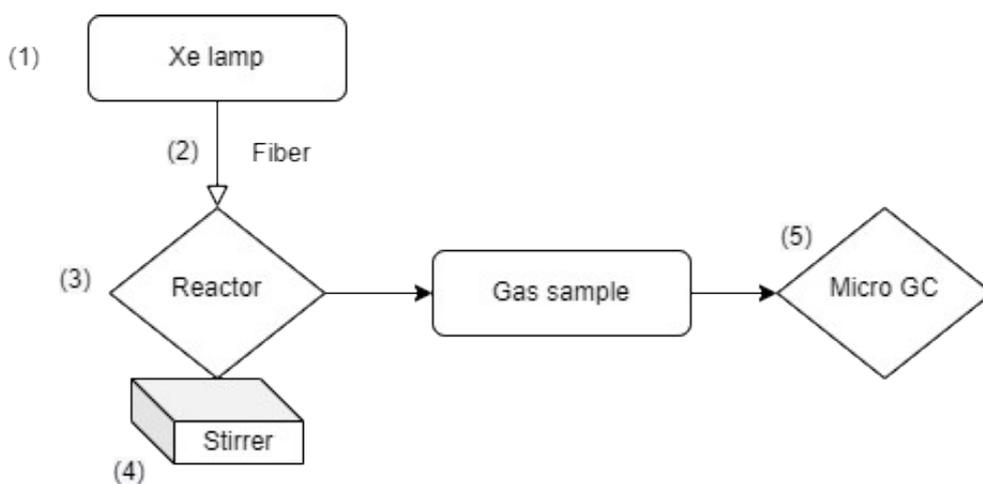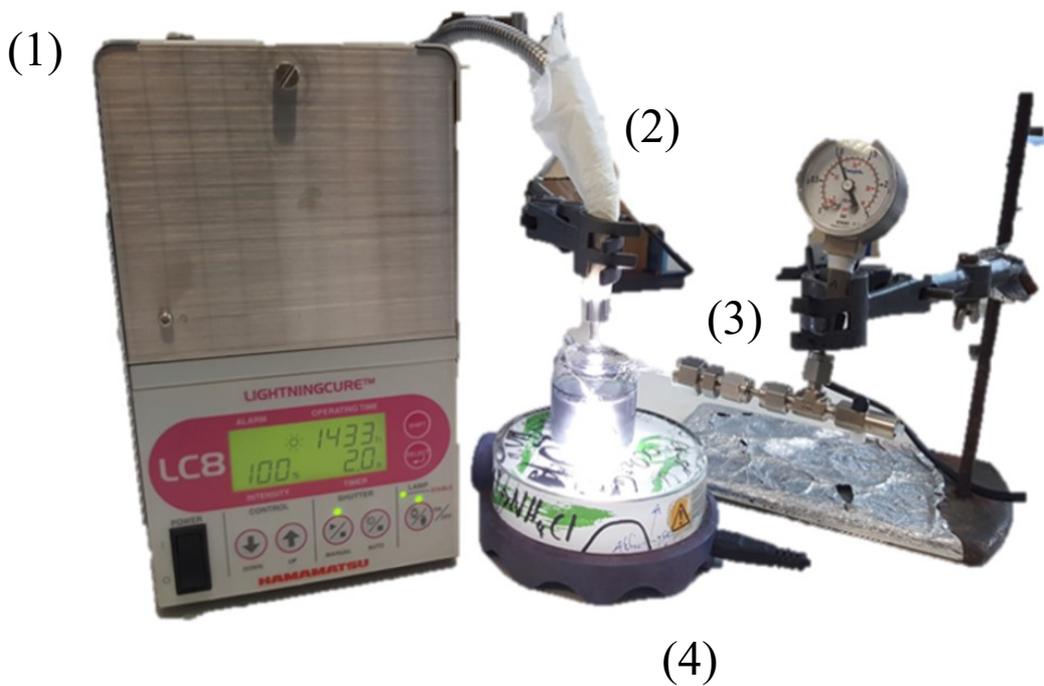
Figure S3. Comparison of the PXRD (A) and XPS (B) of the MIP-177-LT fresh and after photocatalytic FA decomposition. C) SEM images of the used MIP-177-LT sample.
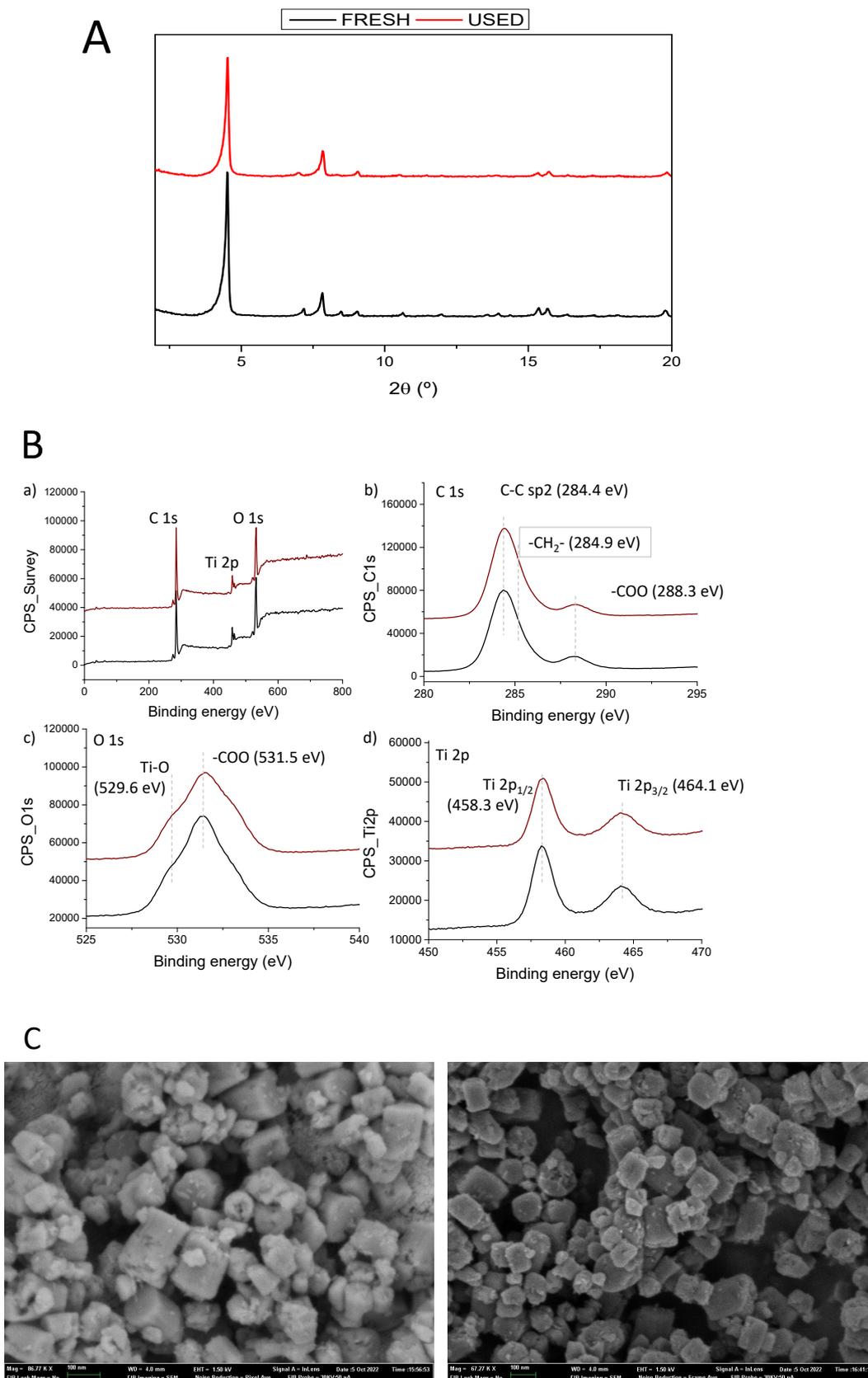
Fig. S4. Temporal profiles of H_2 (black) and CO_2 (red) evolution using as photocatalyst: A: fresh MIP-177-LT sample, B. MIP-177-LT in the second use, and C: MIP-177-LT-AT. Reaction conditions: photocatalyst 10 mg, solution volume 20 mL, FA concentration 10^{-3} M, 300 W Xe lamp through Pyrex. The lines do not correspond to any fitting to a kinetic model.
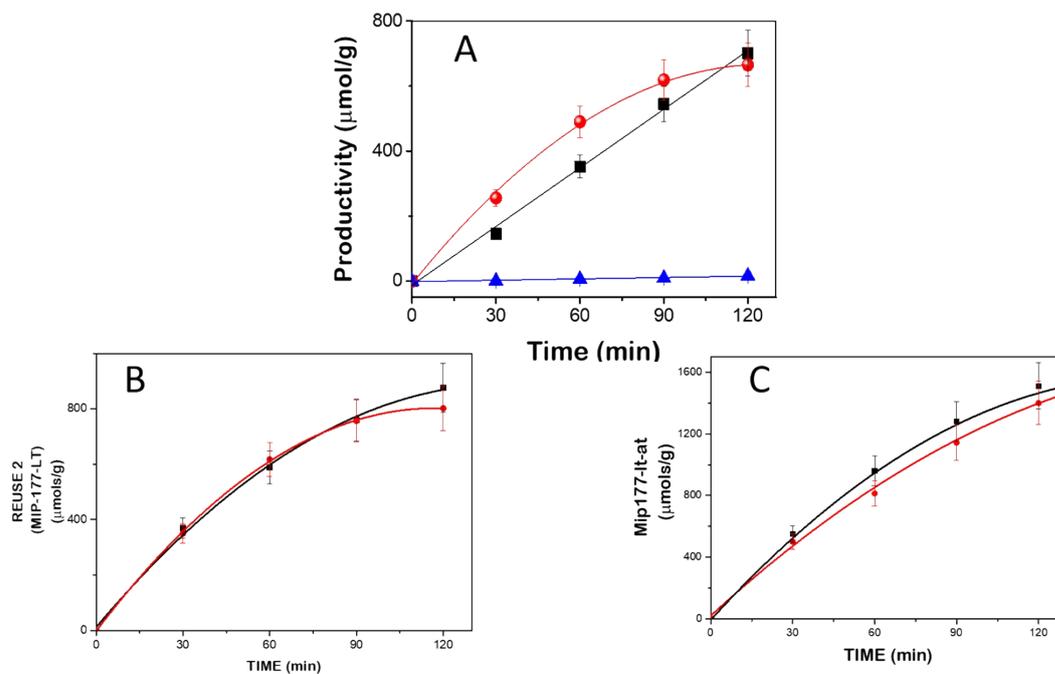
Figure S5. Comparison of the PXRD patterns of the fresh and five times used MIP-177-LT-AT sample.
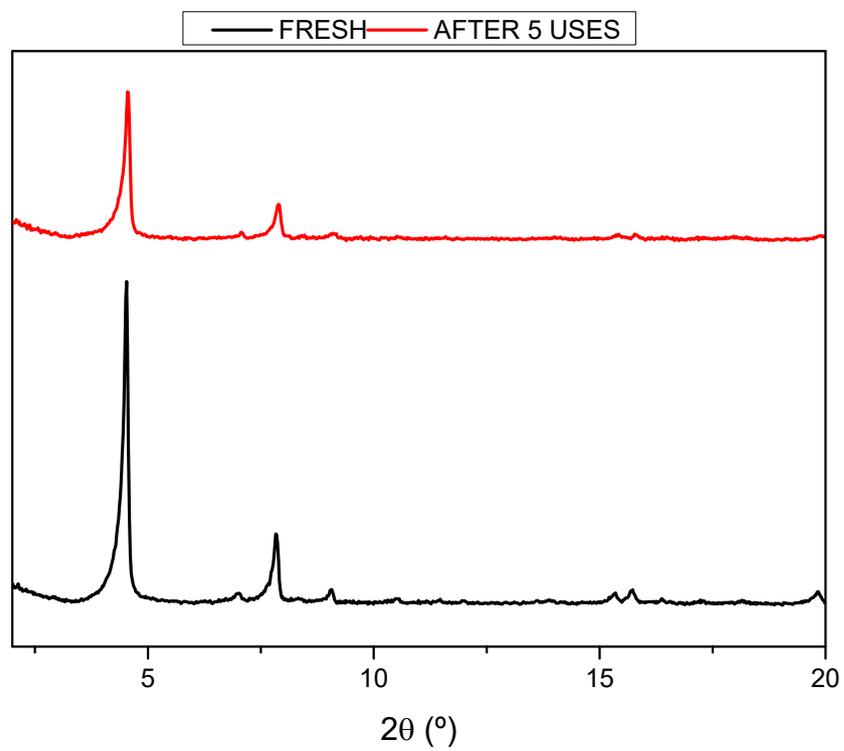
Fig. S6. Relative photocurrent response of MIP-177-LT (red), MIL-15(Ti) (blue) and UiO-66 (black). Measurement conditions: Working electrode: a thin layer of 1 mg of MOF in 1⨯1 cm^2 on FTO electrode. Pt and AgCl/Ag as counter and reference electrode. Single cell with 0.1 M Bu$_4$NPF$_6$ electrolyte. The system was outgassed with Ar 1 h before the measurements. Polarization bias: -1 V. Irradiation: 150 W Xe lamp. Light on/off cycles of 10 s. Note that the maximum photocurrent is related to the extracted electrons from the MOF.
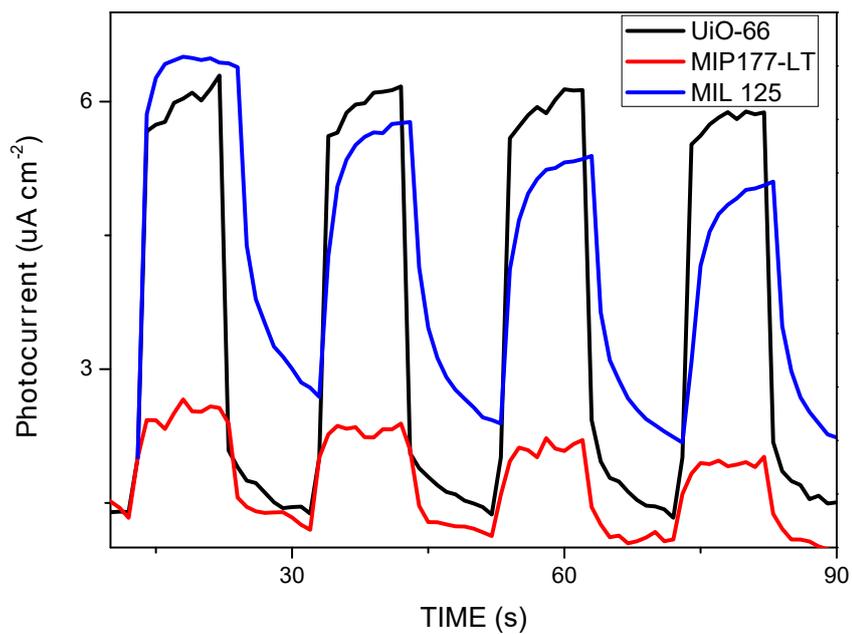
Figure S7. Arrhenius plots of the natural logarithm of the initial reaction rate of H_2 evolution against the reciprocal of the inverse absolute temperature in the range from 125 to 40 °C for MIP-177-LT (A) and TiO_2 (B). Reaction conditions: photocatalyst 10 mg, solution volume 20 mL, FA concentration 10^{-3} M, 300 W Xe lamp through Pyrex.
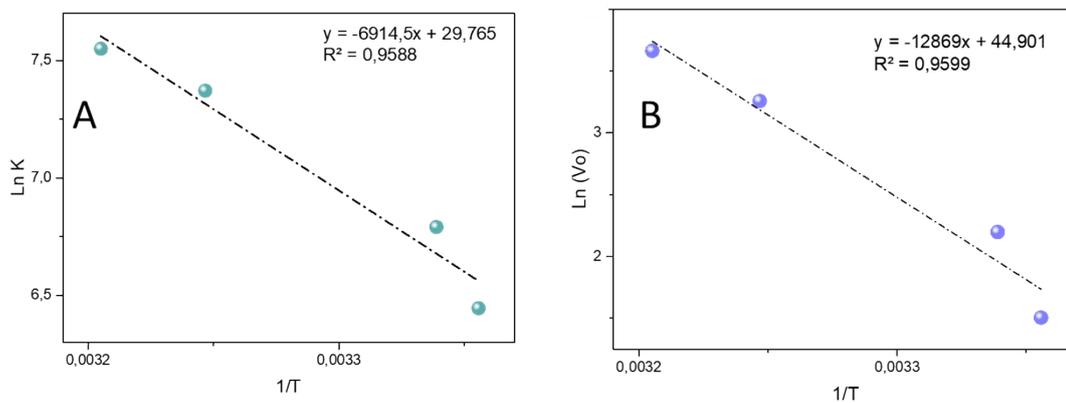
Figure S8. Simulated Gibbs Free Energy Profile for the decarboxylation and dehydration reaction pathways of formic acid.
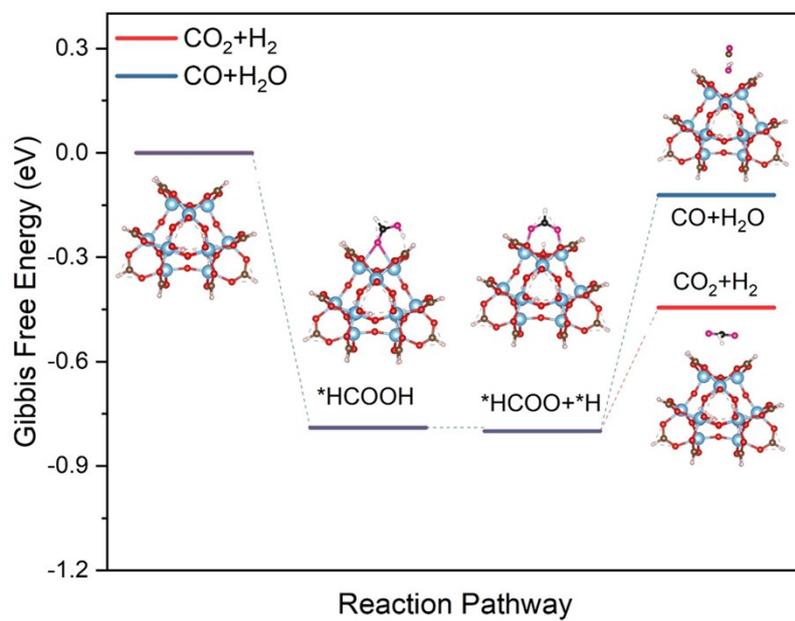
*Figure S9. (a) Substrate of *HCOOH on MIP-177(Ti)-LT cluster model. (b) Substrate of *HCOO on MIP-177(Ti)-LT cluster model. The angels of C-Ti-C are shown for each substrates.*
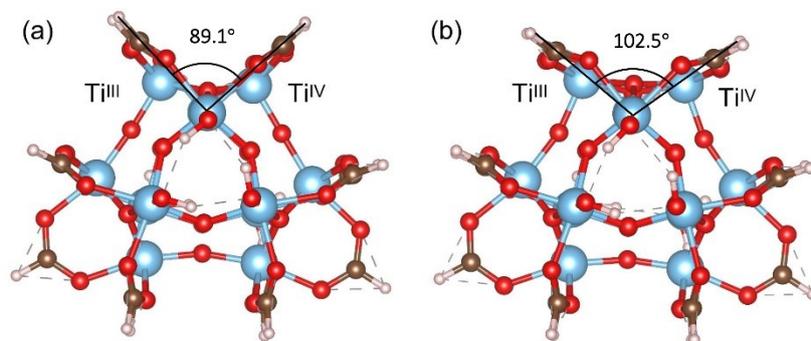
Figure S10. (a) Charge density difference of *HCOOH on MIP-177(Ti)-LT cluster model. (b) Density of states of *HCOOH on MIP-177(Ti)-LT. (c-d) Crystal orbital Hamilton populations analysis of *HCOOH on MIP-177(Ti)-LT for T^{III} and Ti^{IV} adsorption sites. (e) Crystal orbital Hamilton populations analysis of *HCOO on MIP-177(Ti)-LT for Ti^{IV} adsorption site.

Fig. S11. Calibration plots used to quantify CO_2 and H_2 evolution in the gas phase by micro-GC.
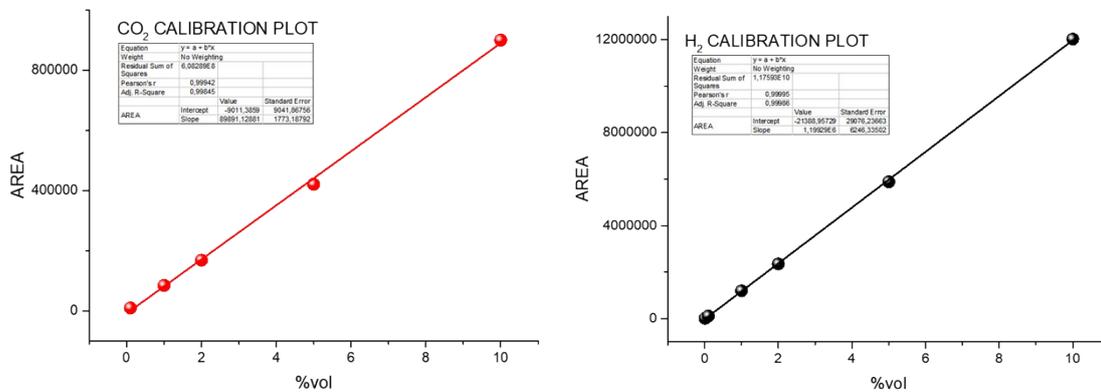
Table S1. Gas evolution upon irradiation of 10 mg of MIP-177-LT and MIP-177-LT-TA as dry powders with the output of a 300 W Xe lamp without filter or filtered light of wavelengths longer than 360 or 400 nm.

MIP-177-LT

Full range

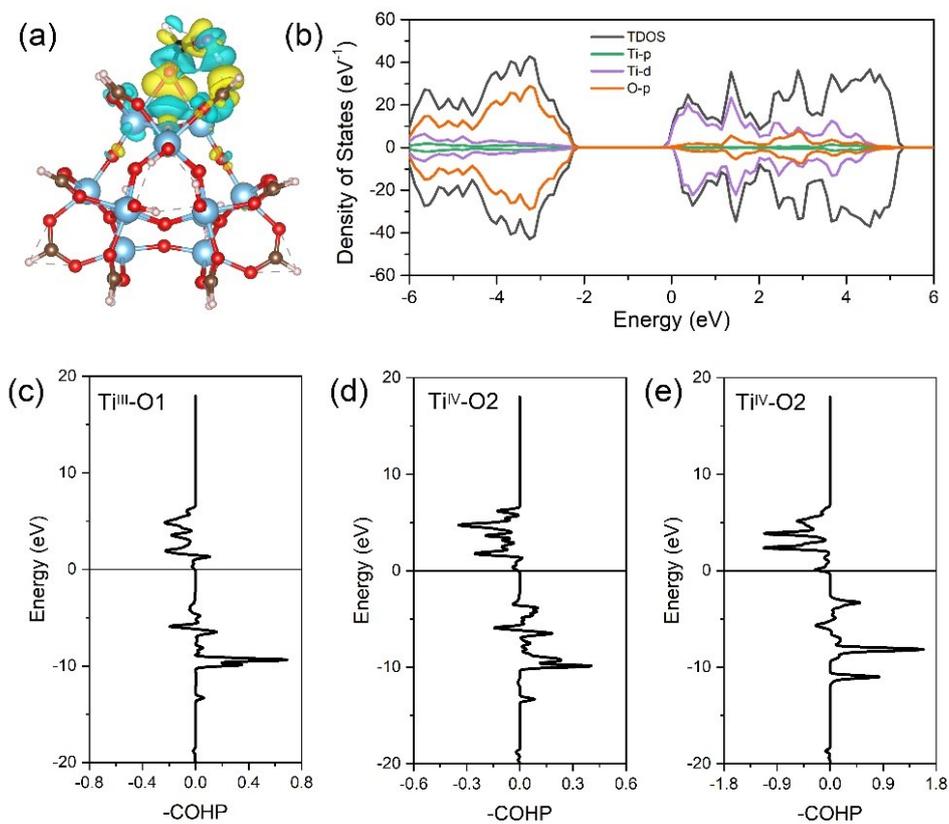| TIME (h)	H_2 (µmols)	CO_2 (µmols)
1	-	2,47
2	-	3,5
24	0,021	8,06

400nm

TIME (h)	H_2 (µmols)	CO_2 (µmols)
0,5	-	0
1	-	0
2	-	0
4	-	1,22
24	-	1,42

360nm

TIME (h)	H_2 (µmols)	CO_2 (µmols)
0,5	-	0
1	-	0
2	-	1,35
4	-	1,38
24	-	2,28

MIP-177-LT-AT

Full range

TIME (h)	H_2 (µmols)	CO_2 (µmols)	CH_4 (µmols)
1	-	1,49	0,085
2,30	0,051	1,80	0,37
4	0,087	2	0,43

400nm

TIME (h)	H$_2$ (µmols)	CO$_2$ (µmols)	CH$_4$ (µmols)
0,5	-	0	0
1	-	-	-
2	-	-	-
4	-	-	-
24	-	1,38	1,539

360nm

TIME (h)	H$_2$ (µmols)	CO$_2$ (µmols)	CH$_4$ (µmols)
0,5	-	0	0
1	-	0,182	0,013
2	-	0,21	0,0243
4	-	-	-
24	0,042	2,81	0,72

Table S1. Photocatalytic H$_2$ evolution rate at different FA concentrations. Reaction conditions: MIP-177-LT 10 mg, solution volume 15 mL, 300 W Xe lamp through Pyrex, room temperature, reaction time 2 h.

(0,01M)

Time (min)	H$_2$(μmols/g)	CO$_2$(μmols/g)	CH$_4$(μmols/g)
60	**274**	428	0
120	**654**	1136	1,54

(1M)

Time (min)	H$_2$(μmols/g)	CO$_2$(μmols/g)	CH$_4$(μmols/g)
60	**290**	689	0
120	**327**	693	0

Table S3. Photocatalytic H_2 release from 10^{-3} M FA solution in the presence of Cerium ammonium nitrate as electron scavenger. *Reaction conditions: MIP-177-LT 10 mg, solution volume 15 mL, Ce(NH$_4$)$_2$(NO$_3$)$_6$ 10^{-3} M, 300 W Xe lamp through Pyrex, room temperature, reaction time 2 h.*

Time (min)	H_2 (μmols/g)	CO_2 (υmols/g)
30	58	600
60	104	680
90	155	742
120	212	794

Table S4. Photocatalytic H_2 release from 10^{-3} M FA solution in the presence of hole scavengers. *Reaction conditions: MIP-177-LT 10 mg, solution volume 15 mL, hole scavenger 10^{-2} M, 300 W Xe lamp through Pyrex, room temperature, reaction time 2 h.*

NaHSO$_3$ as hole scavenger.

Time (min)	H_2 (µmols/g)	CO_2 (µmols/g)
30	140	313
60	345	540
90	490	610
120	700	685

NaHS as hole scavenger.

Time (min)	H2 (µmols/g)	CO2(umols/g)
30	196	366
60	341	427
90	587	544
120	628	627

Table S5. Bond distances between the binding O atoms of *HCOOH or *HCOO and the binding Ti atoms of MIP-177 or $TiO_2(110)$, and the bond distances between the active Ti atoms.

Configurations	$(Ti)Ti^{III}$-O1	$(Ti)Ti^{IV}$-O1(2)	$(Ti)Ti^{III}$-$(Ti)Ti^{IV}$
MIP-177-LT-*HCOOH	2.65	2.61	2.93
MIP-177-LT-*HCOO	2.17	2.16	3.20
$TiO_2(110)$-*HCOOH	2.13	2.18	2.69
$TiO_2(110)$-*HCOO	2.12	2.11	2.80

[1]   G. Kresse, J. Furthmüller, *Computational materials science* **1996**, *6*, 15-50.
[2]   G. Kresse, J. Furthmüller, *Physical review B* **1996**, *54*, 11169.
[3]   J. P. Perdew, K. Burke, M. Ernzerhof, *Physical review letters* **1996**, *77*, 3865.
[4]   S. Grimme, *Journal of computational chemistry* **2006**, *27*, 1787-99.
[5]   Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R., *LOBSTER: A tool to extract chemical bonding from plane-wave based DFT*. Wiley Online Library: 2016.