

Solar Gas-Phase CO₂ Hydrogenation by Multifunctional UiO-66 Photocatalysts

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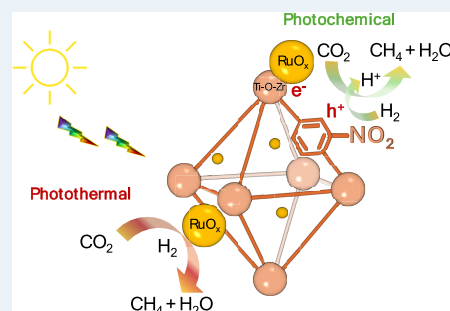
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Supporting Information

ABSTRACT: Solar-assisted CO₂ conversion into fuels and chemical products involves a range of technologies aimed at driving industrial decarbonization methods. In this work, we report on the development of a series of multifunctional metal–organic frameworks (MOFs) based on nitro- or amino-functionalized UiO-66(M) (M: Zr or Zr/Ti) supported RuO_x NPs as photocatalysts, having different energy band level diagrams, for CO₂ hydrogenation under simulated concentrated sunlight irradiation. RuO_x(1 wt %; 2.2 ± 0.9 nm)@UiO-66(Zr/Ti)-NO₂ was found to be a reusable photocatalyst, to be selective for CO₂ methanation (5.03 mmol g^{−1} after 22 h; apparent quantum yield at 350, 400, and 600 nm of 1.67, 0.25, and 0.01%, respectively), and to show about 3–6 times activity compared with previous investigations. The photocatalysts were characterized by advanced spectroscopic techniques like femto- and nanosecond transient absorption, spin electron resonance, and photoluminescence spectroscopies together with (photo)electrochemical measurements. The photocatalytic CO₂ methanation mechanism was assessed by operando FTIR spectroscopy. The results indicate that the most active photocatalyst operates under a dual photochemical and photothermal mechanism. This investigation shows the potential of multifunctional MOFs as photocatalysts for solar-driven CO₂ recycling.

KEYWORDS: heterogeneous photocatalysis, multifunctional metal–organic frameworks: UiO-66 topology, CO₂ methanation, solar light



1. INTRODUCTION

The present level of burning fossil fuels to meet the world's energy requirements is steadily raising the CO₂ emissions released into the atmosphere and is responsible for global warming and climate change.^{1,2} There is thus an urgent need to shift from these fuels to renewable energy obtained from natural resources like the sun, wind, water, or biomass.^{3,4} The development of technologies based on carbon-free energy carriers like green hydrogen is considered vital to help decarbonize the world's economies,^{5,6} whereas carbon capture, storage, and utilization (CCSU) are some processes that can minimize the negative effects of CO₂ emissions.^{7,8} Even though certain CCS processes have achieved relative success, most of the technologies used to convert CO₂ into valuable products or fuels are still under development,^{7–13} including solar-assisted photocatalysis, which is considered to be a promising cost-efficient and sustainable process for recycling CO₂.^{14–19} In 1978, a pioneering study reported on the possibility of reducing CO₂ using GaP as the photoelectrocatalyst.²⁰ Since then, many other inorganic semiconductors^{18,21–24} and, more recently, perovskites,^{23,25} carbon-based materials similar to graphenes,^{23,26,27} or carbon nitrides,^{23,28} among others,^{23,29} have been used for this purpose. H₂ as the reducing agent seems to be more suitable for achieving better performance

than H₂O.³⁰ Because it is expected that green hydrogen will be economically feasible in the medium and long term, this innovation will boost the large-scale production of compounds and fuels from CO₂ hydrogenation.³¹ Of these, the photocatalytic solar-driven reduction of CO₂ by H₂ to CH₄, a process also termed as the *photocatalytic Sabatier reaction*, is attracting increasing interest for the transition to zero net emissions.^{32–34} This process considerably improves the efficiency of the thermocatalytic reaction even when working under mild reaction conditions.³² For example, photocatalytic CO₂ methanation can be carried out at much lower reaction temperatures (~200 °C)²⁵ than the thermocatalytic version (300–350 °C) while achieving similar results.^{25,32} The synthetic methane thus obtained can then be directed to the existing natural gas infrastructures to minimize its implementation costs.³³ To a lesser extent, other related studies have also

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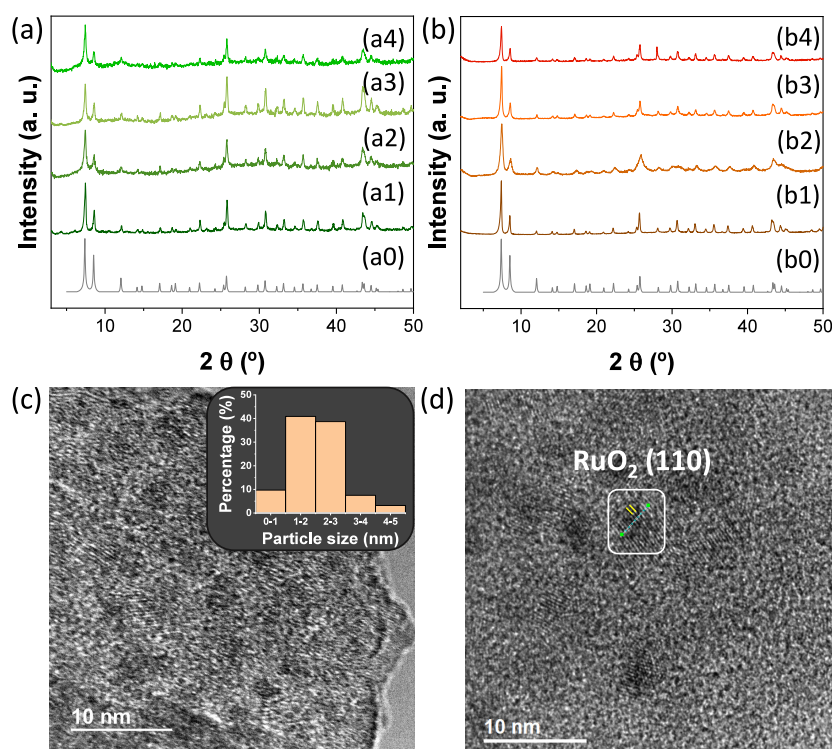


Figure 1. XRD of simulated UiO-66 (a0, b0) or PXRD of UiO-66(Zr)-NH₂ (a) or UiO-66(Zr)-NO₂ (b) materials. Legend panel a: UiO-66(Zr)-NH₂ (a1), RuO_x@UiO-66(Zr)-NH₂ (a2), UiO-66(Zr/Ti)-NH₂ (a3), and RuO_x@UiO-66(Zr/Ti)-NH₂ (a4). Legend panel b: UiO-66(Zr)-NO₂ (b1), RuO_x@UiO-66(Zr)-NO₂ (b2), UiO-66(Zr/Ti)-NO₂ (b3), and RuO_x@UiO-66(Zr/Ti)-NO₂ (b4). (c) HRTEM image and RuO_x particle size distribution of RuO_x@UiO-66(Zr/Ti)-NO₂; RuO_x average particle size and standard deviation of 2.08 ± 0.82 nm. (d) *d*-spacing is determined (0.32 nm) from the HRTEM image of RuO_x@UiO-66(Zr/Ti)-NO₂.

shown the possibility of performing the photocatalytic CO₂³⁰ or CO³⁵ hydrogenation into C₂₊ and even C₅₊ value-added chemicals and fuels.

A relatively new emerging research field for solar-driven photocatalytic Sabatier reaction using metal–organic frameworks (MOFs).³⁶ is under development. MOFs are porous crystalline materials built from multitopic organic ligands coordinated to metal ions, metal clusters, or metal-oxo chains.^{37–39} For about 20 years, MOFs have been considered as highly tunable photocatalysts for many organic and inorganic reactions.^{31,40–42} In the field of CO₂ photoreduction, most of the knowledge achieved so far has come from the liquid-phase reaction using organic solvents in the presence of sacrificial electron donors under UV–vis or visible light irradiation.⁴⁰ Acetonitrile is frequently used as a solvent to favor CO₂ dissolution, whereas triethanolamine is employed as the electron donor to recover photogenerated holes, minimize electron–hole recombination, and thus increase the efficiency of the reduction process.⁴⁰ These studies on MOFs represent an interesting area of research in understanding the theoretical and practical aspects of CO₂ conversion.

A series of recent studies have reported on using MOFs as photocatalysts for gas-phase CO₂ reduction by H₂ under interesting reaction conditions for large-scale processes. The possibility of using MOF-based materials for the photocatalytic gas-phase Sabatier reaction under UV–vis at 215 °C³⁶ was reported for the first time in 2019. Since then, other studies have described a process with MOF-based photocatalysts modified with RuO_x NPs for solar-assisted CO₂ methanation at 200 °C. RuO_x NPs are the benchmark cocatalyst in achieving high efficiency during CO₂ (photo)methanation.³² Some of

these photocatalysts include Ti-MOFs, such as MIP-208(Ti)⁴³ or MIL-125(Ti)-NH₂⁴⁴ functionalized with NH₂ groups. The presence of amino groups determines the MOF energy band level, i.e., a band gap reduction and a negative shift of the lowest unoccupied crystal orbital (LUCO) with respect to the nonfunctionalized parent MOF, and favors the thermodynamics of the reduction processes.^{45,46} Other studies have reported that amino groups in MOFs favor the stabilization of photogenerated holes and, in turn, the photoinduced charge separation efficiency.^{47,48} Amino-MOFs like UiO-66(Zr)-NH₂ have a higher CO₂ adsorption capacity than the analogous UiO-66(Zr)-NO₂ due to the bonding capacity of the amino groups.⁴⁹ Despite the research on the possibility of tuning the energy band diagram of MOFs with functional groups other than amino groups, such as nitro, bromo, or methyl groups, and their resulting photocatalytic activity, few studies have to date addressed its influence on photocatalytic CO₂ hydrogenation.^{45,50,51} Other related studies have shown that mixed-metal MOFs involve higher photocatalytic activity in CO₂ reduction.^{45,52} For example, the better performance of the UiO-66(Zr/Ti)-based photocatalyst than UiO-66(Zr) is associated with the role of Ti(IV) as the electron mediator that favors photoinduced ligand-to-metal charge transfer (LMCT) processes from the organic ligand to the metal node.^{52,53} Despite these important findings, as far as we know, no studies have yet explored the possibility of developing multifunctional MOF-based materials with a unique energy band diagram determined by the presence of specific functional groups, e.g., the amino or nitro groups, simultaneously containing mixed-metal nodes for more effective photoinduced

charge separation and cocatalysts to boost the solar-assisted photocatalytic Sabatier reaction.

In this context, we report here the development of multifunctional nitro- or amino functionalized Zr(IV)- or Zr(IV)/Ti(IV)-based-MOFs with a UiO-66 topology-supported RuO_x NPs for the solar-driven solid–gas phase Sabatier reaction. The materials were characterized by powder X-ray diffraction (PXRD), analytical, spectroscopic, and electron microscopy techniques, and their photocatalytic activities were tested under simulated concentrated sunlight irradiation. Femto- and nanosecond transient absorption (TAS), photoluminescence (PL), electron spin resonance (ESR), and electrochemical impedance (EIS) spectroscopies together with transient photocurrent measurements and additional specific photocatalytic experiments were used to determine the role of MOF counterparts during CO₂ photomethanation via a likely dual photochemical and photochemical mechanism. The photocatalytic CO₂ hydrogenation pathway was studied by operando FTIR spectroscopy.

2. EXPERIMENTAL SECTION

Details of the materials, preparation, characterization, and photocatalytic procedures used in the study can be found in the [Supporting Information](#) (Sections S1–S3).

2.1. Materials, Preparation Methods, and Characterization. All the materials employed in this study were of analytical or HPLC grade and supplied by Merck. UiO-66(Zr)-NH₂ and UiO-66(Zr)-NO₂ were prepared according to previous procedures^{54–56} and were postsynthetically modified by a titanium(IV) chloride tetrahydrofuran complex [TiCl₄(THF)₂] complex to obtain UiO-66(Zr/Ti)-NH₂ and UiO-66(Zr/Ti)-NO₂ as reported.^{57,58} RuO_x NPs were supported on these four UiO-66 solids using the photo-deposition method.⁴⁴

The solids were characterized by PXRD, UV–vis diffuse reflectance (UV–vis DRS), X-ray photoelectron (XPS), electron spin resonance (ESR), steady-state PL, EIS, femto- and nanosecond TAS spectroscopies, and electron microscopy, including transmission electron microscopy (TEM) or scanning transmission electron microscopy (SEM) coupled with an energy-dispersive X-ray electron (EDX) detector. Isothermal N₂ adsorption, thermogravimetric, and photoelectrochemical measurements were also used.

2.3. Photocatalytic Activity. Photocatalytic reactions were carried out under batch reaction conditions ([Section S3](#)), and the data given here are the average of at least three separate experiments.

3. RESULTS AND DISCUSSION

3.1. Photocatalyst Characterization. The MOF-based materials prepared, i.e., UiO-66(M)-X (M: Zr and/or Ti; X: NH₂ or NO₂), both loaded or unloaded with RuO_x NPs, were characterized by different techniques. PXRD analyses revealed that these solids had the expected UiO-66 topology ([Figure 1](#)).⁵⁶ The ICP-OES analyses of acid-digested MOFs were used to quantify the zirconium and/or titanium elements, either loaded or not loaded with RuO_x NPs at 1 wt % of ruthenium. UiO-66(Zr/Ti)-NH₂ and UiO-66(Zr/Ti)-NO₂ have a titanium content of 0.9 and 1.3 wt %, respectively. In this regard, previous studies reported that postsynthetic modification (PSM) of UiO-66(Zr) based materials with TiCl₄(THF)₂ complex results in the incorporation of Ti(IV) in the solid

by metal exchange and/or grafting onto the metal node at the linker vacancy.⁵⁹ Partial replacement of Zr(IV) by Ti(IV) ions with smaller ionic radii contracts the unit cell reflected in PXRD by a small negative shift of the position of the diffraction peaks. In the present work, UiO-66(Zr/Ti)-X (X: NH₂ or NO₂) solids showed similar PXRD peak positions to those in zirconium, indicating that Ti(IV) ions are mostly grafted onto the MOF metal nodes.^{57,59} The PXRD of UiO-66 solids loaded with RuO_x NPs have similar features to those of the parent MOFs. The absence of RuO_x diffraction peaks was attributed to the low ruthenium loading (1 wt %) in the MOF and/or good dispersion of small NPs.⁴⁴

The HR-SEM analyses showed that UiO-66 crystals are characterized by the agglomeration of small cubes with average particle sizes and standard deviations of 118 ± 57 nm ([Figure S1](#)). HR-SEM in combination with EDX analyses ([Figures S2–S10](#)) showed a good distribution of MOF elements within the particles. The relatively low intensity of ruthenium due to its low loading (1 wt % Ru) was within the instrument's detection limit. DF-STEM coupled with EDX and HR-TEM measurements characterized RuO_x NPs (2.14 ± 0.86 nm) supported on UiO-66 particles. HRTEM measurements ([Figures S11–S14](#)) indicated the presence of 0.32 nm lattice spacings ([Figures S15–S17](#)), characteristic of the (110) facet of RuO₂.⁶⁰

The UiO-66 samples were also characterized by XPS ([Figure 2](#) and [Figures S18–S21](#)) to determine the oxidation state of the elements within the solids. The XPS spectra of the C 1s

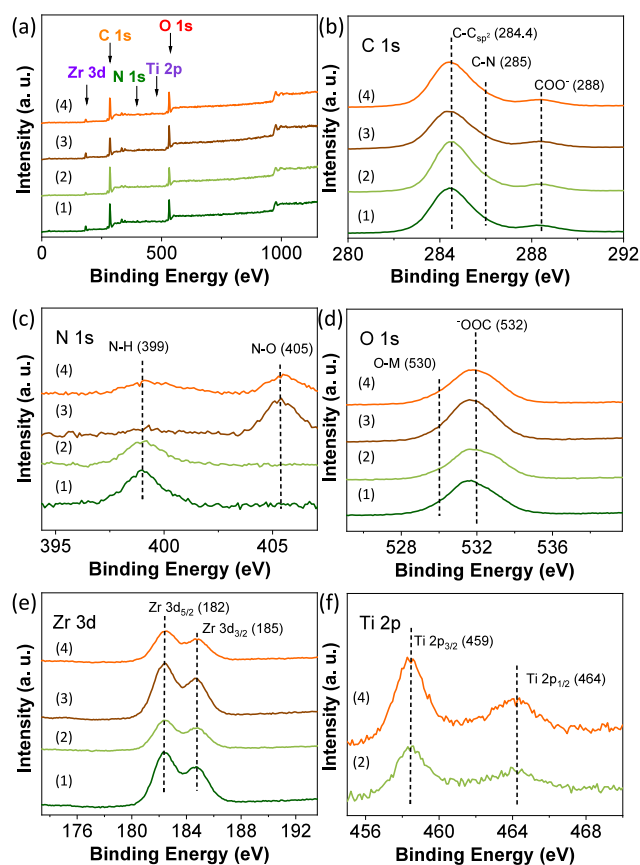


Figure 2. XPS survey (a), C 1s (b), O 1s (c), N 1s (d), Zr 3d (e), and Ti 3p (f) of UiO-66(Zr)-NH₂ (1), UiO-66(Zr/Ti)-NH₂ (2), UiO-66(Zr)-NO₂ (3), and UiO-66(Zr/Ti)-NO₂ (4).

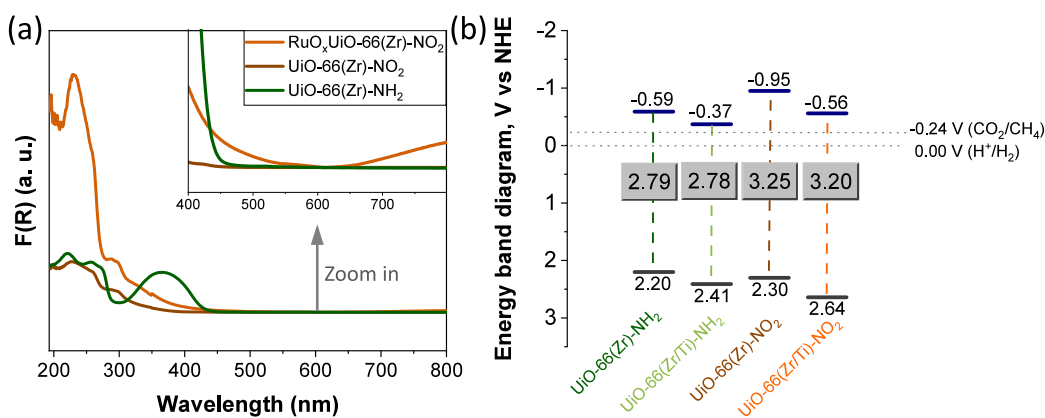


Figure 3. (a) UV-vis DRS and (b) energy band level diagram of UiO-66 solids as indicated.

region are associated with the presence of the 2-amino or 2-nitroterephthalates ligands of the MOFs: C–C sp^2 bonds (284.4 eV), COO^- groups (288 eV), and C–N bonds of amino or nitro (~ 285 eV) groups. The N 1s XPS of amino-functionalized UiO-66 solids shows the expected C–N signal at about 399 eV. In the case of nitro-functionalized UiO-66 materials, N 1s XPS spectra are dominated by a main band at 405 eV due to the nitro group, whereas a signal associated with the presence of an amino group can also be detected. This situation, i.e., the presence of a small band assigned to the amino group when preparing nitro-functionalized UiO-66 solids, has previously been reported.⁵¹ For the series of RuO_x NPs supported UiO-66 solids, the XPS Ru 3d spectra showed a weak band centered at about 282 eV (Figures S22 and S25), partially overlapping with C–C sp^2 bond signals (284.4 eV), which can be assigned to the presence of RuO_2 NPs.⁴⁴ Supported RuO_2 NPs were further characterized by Ru 3p XPS, where the expected two bands could be seen at about 462.5 and 485 eV characteristic of Ru $3p_{3/2}$ and Ru $3p_{1/2}$, respectively. The O 1s XPS signal was assigned to the presence of COO^- groups (532 eV) and M–O bonds (M: Zr, Ti or Ru) (530 eV). Zr 3d and Ti 2p XPS spectra showed the expected signals of Zr(IV) and Ti(IV) ions in the UiO-66 structure. Zr 3d XPS spectra had two bands centered at about 182 and 185 eV due to Zr $3d_{5/2}$ and Zr $3d_{3/2}$, respectively. The XPS spectra of the Ti 2p region for mixed-metal UiO-66(Zr/Ti)-X (X: NH_2 or NO_2) confirmed the presence of Ti(IV) indicated by two bands at 459 and 464 eV due to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively.

The UiO-66 solids were analyzed by FTIR spectroscopy (Figure S26). In all cases, COO^- groups were characterized by stretching vibrations at about 1574 and 1423 cm^{-1} , respectively. Amino-functionalized UiO-66 solids showed two bands at 3488 and 3374 cm^{-1} due to the asymmetric and symmetric vibrations of $-NH_2$, respectively, together with another band at 1255 cm^{-1} due to C–N stretching vibration. In the case of nitro-functionalized UiO-66 solids, two bands could be seen at about 1543 and 1496 cm^{-1} due to the characteristic asymmetric and symmetric vibration bands of this group, respectively. These spectra also showed small bands attributable to the presence of amino groups, in good agreement with the XPS analyses. These XPS and FTIR results indicate a need for the development of new synthetic methodologies to prepare UiO-66 solids with only 2-nitroterephthalate ligands in their structure.

Isothermal N_2 adsorption measurements were used to estimate the BET surface areas (Figure S27) and pore volumes of pristine mono- and bimetallic UiO-66 solids with values ranging from 600 to 700 m^2/g and 0.23 to 0.26 cm^3/g , respectively, in agreement with previous studies.⁵⁷ TGA analyses under oxidant (air) or inert (nitrogen) atmospheres further confirmed that these UiO-66 samples are thermally stable at temperatures of about 300 $^\circ C$, and these observations are in agreement with previous reports (Figure S28).^{57,61,62} It should be commented that the stability observed below 300 $^\circ C$ under these atmospheres might differ somehow the stability under the reaction conditions of photocatalytic CO_2 hydrogenation (H_2/CO_2 molar ratio 4:1 at 200 $^\circ C$). Additionally, a control experiment revealed that the TGA of UiO-66(Zr/Ti)- NO_2 solid previously submitted to these reaction conditions exhibited a very similar TGA profile under air than the fresh sample, thus confirming its relative stability under studied reaction conditions.

The optical properties of the UiO-66 materials were studied by UV-vis DRS measurements. Figure 3 shows that the presence of NO_2 and especially NH_2 groups in the MOF organic ligand favors visible light absorption with absorption onsets at about 400 and 450 nm, respectively. In the case of amino-functionalized UiO-66 solids, the band centered at about 365 nm is due to the interaction of the lone pair of electrons of amino group with the π^* -orbital of aromatic ring, and this situation results in a new higher HOCO level that favors visible light absorption.⁶³ Tauc plot analyses using the UV-vis DRS data (Figure S29) confirmed that the optical band gaps of amino-functionalized UiO-66 solids were lower than those of the nitro-functionalized UiO-66 solids.⁶⁴ Besides, mixed-metal UiO-66 solids exhibit somehow lower optical band gaps associated with the role of Ti(IV) ions as electron mediators in agreement with previous experimental^{48,58} and theoretical studies.⁶⁵ XPS valence band measurements (Figure S30) were used to estimate the UiO-66 energy band diagrams together with the optical band gaps. In general, all the solids possessed the thermodynamic requirements for photocatalytic CO_2 hydrogenation under sunlight irradiation, whereas the UV-vis DRS of RuO_x NPs on UiO-66 solids showed an extra weak absorption band in the visible region associated with the resonance plasmon band of these NPs (Figure S31).

3.2. Photocatalytic CO_2 Hydrogenation. UiO-66-based solids were first tested as photocatalysts for CO_2 hydrogenation at 200 $^\circ C$ under simulated concentrated sunlight irradiation (200 mW/cm^2). For this purpose, the quartz

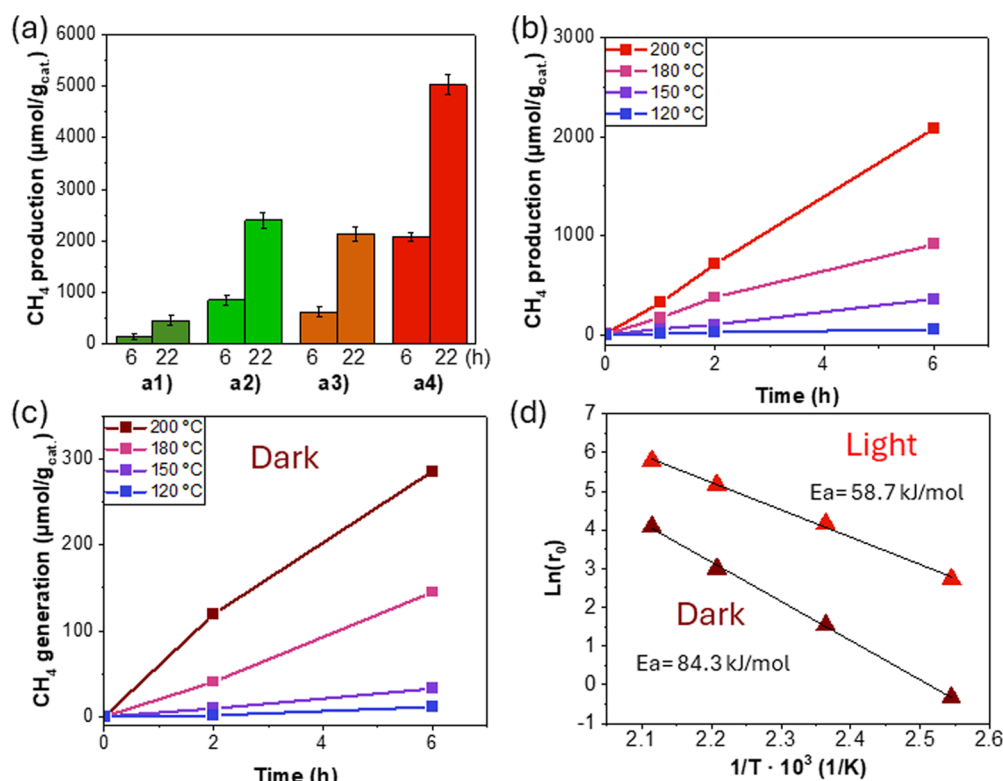


Figure 4. (a) Photocatalytic CO_2 methanation using $\text{RuO}_x/\text{UiO-66}$ solids under simulated concentrated sunlight irradiation. Legend: (a1) UiO-66(Zr)-NH_2 , (a2) $\text{UiO-66(Zr/Ti)-NH}_2$, (a3) UiO-66(Zr)-NO_2 , and (a4) $\text{UiO-66(Zr/Ti)-NO}_2$. Influence of reaction temperature on methane generation during photocatalytic CO_2 reduction under light (b) or dark (c) conditions. (d) The Arrhenius plot obtained from initial reaction rates of methane generation as a function of the reaction temperature under dark or light conditions as indicated. Reaction conditions: photocatalyst (15 mg), CO_2/H_2 (1:4), 200 °C, simulated concentrated sunlight ($200 \text{ mW}/\text{cm}^2$) irradiation.

reactor is heated with a mantle, and then the system was irradiated (see details in Section 2). It should be remembered that 1 sun is defined as $100 \text{ mW}/\text{cm}^2$ of irradiance. From the point of view of practical applications, solar concentrators could be used to reach the simulated concentrated sunlight irradiations used in this study. Pristine UiO-66 solids showed little activity, and methane was the only product detected ($<30 \mu\text{mol g}^{-1}$). Specifically, to illustrate the importance of supported RuO_x NPs in enhancing the photocatalytic activity, the performance of UiO-66(Zr)-NH_2 , $\text{UiO-66(Zr/Ti)-NH}_2$, UiO-66(Zr)-NO_2 , and $\text{UiO-66(Zr/Ti)-NO}_2$ was evaluated and observing only 2, 13, 3, and $4 \mu\text{mol g}^{-1}$ after 22 h, respectively. However, RuO_x NPs supported UiO-66 materials boosted activities toward methane generation by various degrees, in agreement with the role of RuO_x NPs as benchmark cocatalysts for selective CO_2 (photo)catalytic methanation.³² RuO_x NPs have the ability to favor chemisorption CO_2 and its reaction intermediates like CO or H_2CO with sufficient strength to be completely hydrogenated to methane.³⁴ Even though our analyses allow identification and quantification of several carbon products such as CO or short-chain hydrocarbons (see Supporting Information Section S3), methane was the main product together with small amounts of ethane detected for all tested photocatalysts. In other words, all (photo)catalytic tests carried out in this study resulted in methane selectivities higher than 99%. Control experiments in which CO_2 was replaced by Ar did not indicate the formation of methane or any other product. Because of the similar particle size distribution of RuO_x NPs supported on UiO-66 solids, i.e., a mean average particle size and standard deviations of $2.14 \pm 0.04 \text{ nm}$, we

consider that the composition of the UiO-66 photocatalysts determines the resulting activities. Furthermore, it was found that product selectivity is not influenced by the use of UiO-66 composition loaded or not with RuO_x NPs. As an example, the product selectivity distribution of the most active $\text{RuO}_x/\text{UiO-66(Zr/Ti)-NO}_2$ indicates a CH_4 selectivity higher than 99% accompanied by ethane. Figure 4 shows that nitro-functionalized UiO-66 photocatalysts are more active than amino-functionalized UiO-66 photocatalysts. This is an important finding because, as commented in the introduction, amino-functionalized MOFs like UiO-66 are among the preferred solids for photocatalytic applications, including CO_2 reduction. Regardless of UiO-66(Zr)-NO_2 's higher optical band gap than UiO-66(Zr)-NH_2 (3.16 vs 2.79 eV), its better reduction and oxidation capacity than those of the amino group seems to determine its photocatalytic activity (see Figure 3). Figure 4 also shows that the photocatalytic activities of RuO_x NPs supported UiO-66(Zr)-X (X: NH_2 or NO_2) are further increased by the preparation of analogous mixed-metal Zr/Ti materials. Previous studies have demonstrated the role of Ti(IV) ions in the metal node of $\text{UiO-66(Zr/Ti)-NH}_2$ as photoinduced electron transfer mediators.^{48,58} As will be shown below, the better performance of mixed-metal UiO-66 photocatalysts supported by RuO_x NPs than those analogous monometallic ones can be attributed to the increased photoinduced charge separation efficiency, as shown by the spectroscopic and electrochemical characterization.

To further verify the role of nitro or amino groups in UiO-66(Zr)-X (X: NO_2 or NH_2) on the resulting photocatalytic activity, an analogous photocatalyst termed as UiO-66(Zr) was

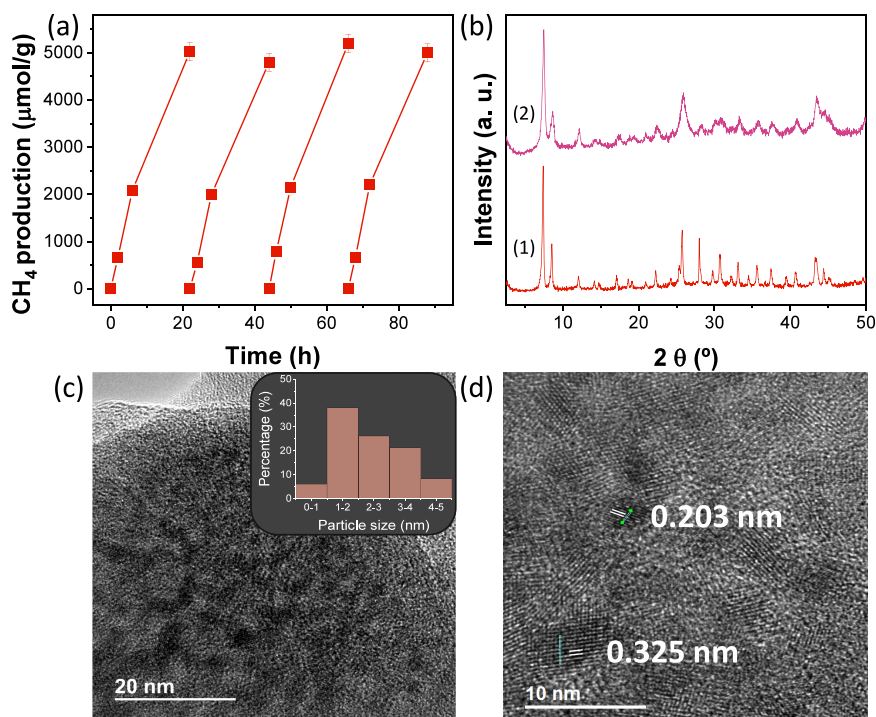


Figure 5. (a) Reusability of RuO_x@UiO-66(Zr/Ti)-NO₂ during photocatalytic CO₂ methanation. (b) PXRD of RuO_x@UiO-66(Zr/Ti)-NO₂ fresh (1) and used (2). (c) TEM image and particle size distribution of used photocatalyst. (d) HRTEM for interplanar distance.

prepared using terephthalic acid as organic ligand and further modified with RuO_x NPs by the photodeposition method. The samples were characterized by PXRD, spectroscopic (UV–vis, XPS), analytical (TGA), textural (isothermal N₂ adsorption), and electron microscopic techniques (Figures S32–S37). PXRD confirmed that RuO_x@UiO-66(Zr) and UiO-66(Zr) samples are isostructural crystalline materials with UiO-66 topology (Figure S32). XPS analyses revealed the general expected features of XPS C 1s, O 1s, Zr Ru 3d, and 3p (Figure S33). These solids are constituted by particles of 98 ± 63 nm as revealed by SEM analyses (Figure S34). TEM measurements revealed the presence of supported RuO_x NPs with sizes of 2.4 ± 0.8 nm (Figure S35). The sample exhibited good porosity ($1008 \text{ m}^2/\text{g}$ and $0.38 \text{ cm}^3/\text{g}$) and thermal stability under air atmosphere ($>400^\circ\text{C}$) (Figure S36). The energy band level diagram of UiO-66(Zr) is characterized by a wide optical band gap (3.7 eV) with HOCO and LUCO positions of +1.81 and -2.15 V, respectively (Figure S37). The use of RuO_x@UiO-66(Zr) and pristine UiO-66(Zr) as photocatalysts under conditions described in Figure 4 showed a selective methane production of 500 and 2 μmol g^{-1} , respectively, after 22 h. The activity of this RuO_x@UiO-66(Zr) photocatalyst is slightly lower than that of RuO_x@UiO-66(Zr)-NH₂ and about three times lower than that achieved using the RuO_x@UiO-66(Zr)-NO₂ photocatalyst. Regardless of the lower CO₂ adsorption capacity and higher optical band gap of UiO-66(Zr) compared to UiO-66(Zr)-NH₂, their photocatalytic activities are similar to each other. In contrast, as previously commented, RuO_x@UiO-66(Zr)-NO₂ exhibits higher activity associated with its unique structure due to the presence of nitro functional groups. The performance of the most active RuO_x@UiO-66(Zr/Ti)-NO₂ sample ($\sim 13\%$ CO₂ conversion; $5.03 \text{ mmol}_{\text{CH}_4} \cdot \text{g}^{-1}$ after 22 h) during photocatalytic CO₂ hydrogenation to CH₄ was further studied. A photocatalytic experiment using labeled ¹³CO₂ and gas-phase aliquot analysis

by GC coupled to mass spectrometer using an electron ionization method confirmed the formation of ¹³CH₄ (m/z 17) after 22 h of reaction at 200°C (Figure S38). It should be noted, however, that the characteristic ionization profile of methane differs to some extent to the one obtained and associated with the contribution of other molecules like H₂O and air from ambient during the injection that are not chromatographically separated in our system. As will be shown later in Section 3.3.2, the transformation of CO₂ into CH₄ has been further confirmed by using operando FTIR analyses. A control experiment under dark reaction conditions at 200°C also revealed lower CH₄ production (1.9 mmol g^{-1} after 22 h) than that achieved under simulated concentrated sunlight irradiation. The observation of some activity under dark reaction conditions was not unexpected because previous studies have reported that RuO_x NPs are an active and selective cocatalyst during thermal catalytic processes.³² Quantitative information on the performance of RuO_x@UiO-66(Zr/Ti)-NO₂ as a photocatalyst at 200°C was obtained by estimating the apparent quantum yield (AQY) at specific wavelengths. After deducting the activity observed under dark reaction conditions, the AQYs achieved by irradiation at 350, 400, and 600 nm were 1.67, 0.25, and 0.01%, respectively. The influence of the reaction temperature on the photocatalytic activity of RuO_x@UiO-66(Zr/Ti)-NO₂ was then studied (see results in Figure 4b). As can be seen, photocatalytic methane generation as a function of the reaction temperature follows the Arrhenius law and allowed us to estimate an apparent activation energy (E_a) of 58.7 kJ/mol . In a series of analogous experiments carried out in the absence of irradiation (thermal catalysis), the estimated E_a resulted to be 84.3 kJ/mol . Based on analogous studies^{66–68} and as will be further studied in Section 3.3, this significant decrease in E_a can be attributed to the operation of a photothermal reaction pathway.

The photocatalytic activity of $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ was compared with those MOF-based photocatalysts reported in previous studies, and the results are summarized in Table S1. The use of the same reaction conditions than most of the studies in Table S1, i.e., $P_{\text{H}_2} = 1.05$ bar and $P_{\text{CO}_2} = 0.25$ bar instead the previous $P_{\text{H}_2} = 1.2$ bar and $P_{\text{CO}_2} = 0.3$ bar, resulted in a methane production decrease of about 5% in agreement with Chatelier's principle. RuO_x NPs supported trimetallic UiO-66(Zr/Ce/Ti) was recently reported as one of the most active MOF-based photocatalysts for CO_2 methanation under simulated concentrated sunlight irradiation ($1.8 \text{ mmol g}^{-1} \text{ CH}_4$ after 22 h at 200°C) (Table S1, entry 2), showing that the activity of $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ is about 3 times higher than this photocatalyst under similar reaction conditions. Furthermore, $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ exhibits an activity 3–6 times higher than that achieved using analogous solids based on RuO_x NPs supported on Ti-based MOFs, such as MIL-125(Ti)-NH_2 (Table S1, entries 3 and 4) or MIP-208(Ti) (Table S1, entry 5). It is remarkable that the activity of $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ (Table S1, entry 1) is more than two times compared with $\text{RuO}_x\text{@MIL-125(Ti)-NH}_2$ (Table S1, entry 4) having double the amount of ruthenium (2 wt %). It should be noted that all these photocatalysts have a similar RuO_x NP loading (1 wt % of ruthenium) and an average particle size ($\sim 2 \text{ nm}$). The higher activity of $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ thus appears to be related to the energy band diagram level of the photocatalyst determined by the combination of 2-nitroterephthalates ligands and mixed-metal Zr(IV)/Ti(IV) metal nodes, which boosts the efficiency of the reaction. Regardless of these comments, it is pertinent to mention that the state-of-the-art in current photocatalytic gaseous methanation has reported activities, in some cases, greater than $100 \text{ mmol g}^{-1} \text{ h}^{-1}$. In one of these examples, ultrathin Mg–Al layered double hydroxide nanosheet supported Ru NPs were found to achieve efficient photo-thermal CO_2 methanation ($277 \text{ mmol h}^{-1} \text{ g}^{-1}$; 300 W Xe lamp) under continuous flow operation.⁶⁹

The activity and stability of $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ were studied by performing consecutive reuse experiments. Figure 5 shows that the photocatalyst can be reused without significant loss of activity for four consecutive times with an accumulated reaction time of 90 h. According to PXRD analysis, the crystallinity of the four-times used photocatalyst is preserved. TEM analyses of the reused photocatalyst confirmed that RuO_x average particle size and standard deviation ($2.32 \pm 0.90 \text{ nm}$) are similar compared to the fresh sample ($2.08 \pm 0.82 \text{ nm}$). Besides, HR-TEM characterization of the used photocatalyst revealed the presence of lattice fringes with spacings of about 0.203 and 0.32 nm, which were ascribed to the crystal planes (101) and (110) of Ru(0) and RuO_2 , respectively (Figures S4d and S39).

C 1s, O 1s, Zr 3d, and Ti 2p XPS analyses of the four-times used photocatalyst (Figure S40) showed similar features to those of the fresh material, whereas N 1s and Ru 3d XPS showed small but appreciable differences with respect to the fresh sample (Figure 6 and Figure S41). N 1s XPS of the used photocatalyst revealed slight hydrogenation of the nitro group to the amino group (Figure 5). Specifically, the fresh and used $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ photocatalysts have a proportion in weight percent of NO_2 versus NH_2 of 55.2/44.8 and 46.8/53.2, respectively. Although partial reduction of NO_2 to NH_2 is observed in the used $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ photocatalyst by XPS, the structural integrity of the used

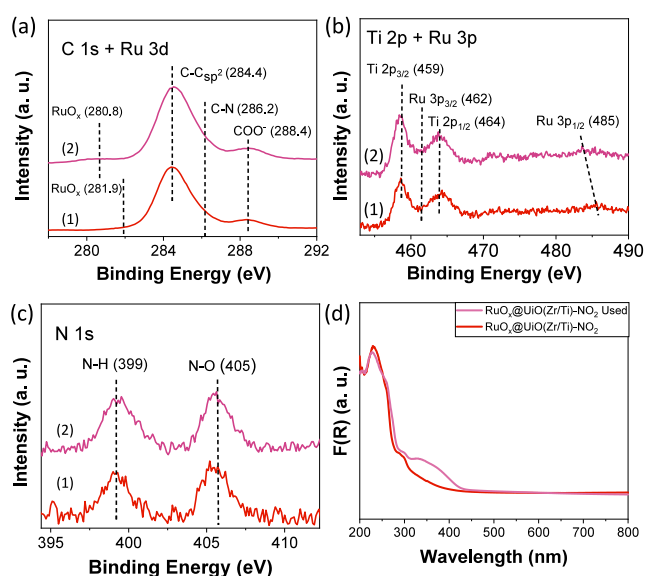


Figure 6. (a) C 1s + Ru 3d, (b) Ti 2p + Ru 3p, (c) N 1s XPS of fresh (1) and used (2) photocatalyst, and (d) UV–vis of fresh and used $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$.

photocatalyst still contains enough NO_2 groups (46.8 at%) to promote the photocatalyst activity without much significant difference (Figure 6). Furthermore, UV–vis DRS of the used sample showed an extra absorption band with onset absorption at about 430 nm, which agrees with the partial nitro hydrogenation to the amino group (Figure 5). In the case of Ru 3d XPS, a small shift of the Ru 3 $d_{5/2}$ was seen toward lower binding energies with respect to the fresh sample (281.9 vs 280.8 eV). These results agree with previous studies that also showed the supported RuO_x NPs employed as cocatalysts during (photo)catalytic hydrogenations at temperatures of about 200°C can be converted to some extent to the metallic phase.^{44,69–72}

In the present study, additional *in situ* XPS experiments in which the fresh $\text{RuO}_x\text{@UiO-66(Zr/Ti)-NO}_2$ sample is submitted to a H_2 thermal treatment at 200°C also revealed that supported RuO_x NPs are susceptible to be partially reduced to metallic NPs under the studied reaction conditions (Figure S42). It should be noted that metallic ruthenium species have been proposed as responsible species to activate molecular H_2 and initiate CO_2 hydrogenation.^{69,70,72,73} Besides, as will be shown later, RuO_x and Ru species also favor CO_2 and CO chemisorption as evidenced by FTIR spectroscopy. Overall, these results demonstrate that RuO_x NPs supported on $\text{UiO-66(Zr/Ti)-NO}_2$ are partially reduced during the photocatalytic CO_2 hydrogenation process, leading to the coexistence of supported RuO_x and Ru(0) species within the photocatalyst.

In the area of photocatalysis using MOFs, some studies have reported UV–vis irradiation of carboxylate-based MOFs at 200°C that resulted in partial decarboxylation.⁷⁴ To address this issue, a photocatalytic control experiment in which CO_2 was replaced by Ar revealed the presence of CO_2 , attributed to the partial decarboxylation of the terephthalate MOF ligand during the reaction (1.8 wt % with respect to the amount of the initial carboxylate). These results indicate a need to develop active MOF-based photocatalysts that can operate under milder reaction conditions with operational stabilities.

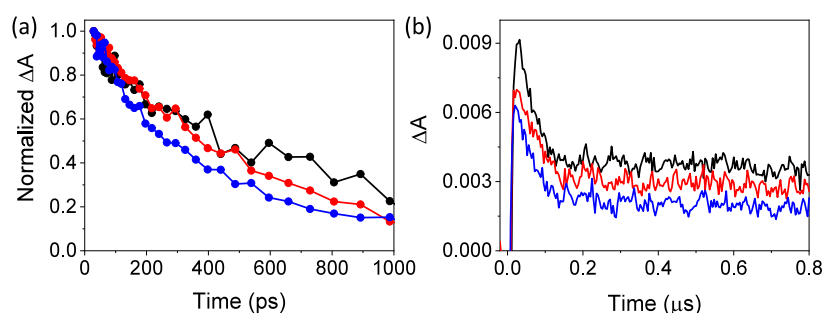


Figure 7. (a) Femtosecond transient absorption recorded at 586 nm and (b) LFP decay traces recorded at 520 nm for UiO-66(Zr)-NO₂ (black), UiO-66(Zr/Ti)-NO₂ (red), and RuO_x@UiO-66(Zr/Ti)-NO₂ (blue). fs-TAS measurements were performed at $\lambda_{\text{exc}} = 267$ nm in aerated MeCN, whereas those of LFP were done at $\lambda_{\text{exc}} = 266$ nm in MeCN under an Ar atmosphere.

3.3. Photocatalytic Reaction Pathways. **3.3.1. Exploration of Photochemical and Photothermal Reaction Mechanisms.** Based on previous reports, photocatalytic CO₂ reduction using metal/metal oxide NPs supported on MOFs or other materials can occur via photochemical^{24,34} and/or photothermal reaction mechanisms.^{24,34,75–77} During the photochemical pathway, the irradiation of the photocatalysts results in the formation of reducing and oxidizing electron and hole pairs, respectively. This is a common reaction mechanism found when using MOFs as photocatalysts when their irradiation by appropriate wavelengths produces photoinduced electron transfer from the organic ligand to the metal node.⁴³ The presence of MNPs like RuO_x as cocatalysts can also favor photochemical pathway efficiency by opening new channels for charge carrier separation and enhancing photocatalytic activity.⁴⁴ RuO_x NPs have also been reported to promote the photothermal reaction pathway in which light energy is transformed into heat, which favors CO₂ methanation.⁷⁵

Several characterization techniques were used to further study these possible reaction pathways using RuO_x NPs supported UiO-66(Zr and/or Ti)-X (X: NH₂ or NO₂). It should be noted that, as shown in Figure 6, the RuO_x@UiO-66(Zr/Ti)-NO₂ photocatalyst used exhibits a partial reduction of supported RuO_x NPs with respect to the fresh sample. To consider the possible influence of the RuO_x oxidation state on the subsequent characterization data, some comparative measurements were carried out using both fresh and used photocatalysts.

To evaluate the photoinduced processes arising from the excitation of the different UiO-66(Zr/Ti)-X (X: NH₂ or NO₂) photocatalysts at 267 nm,^{30,75} these were first studied by femtosecond TAS (fs-TAS). This technique has been shown to be sensitive and precise for investigating processes occurring at a very early stage after excitation, including ultrafast electron transfer or charge separation.⁷⁸ The recorded transient absorption spectra (Figure S43) and kinetics (Figure S44) of UiO-66(Zr)-NH₂ showed good agreement with previously reported observations,⁷⁹ whereas notable differences were found in the transient absorption spectra when using NO₂ (Figure S45). The transient absorbance of the latter samples covers the entire visible spectrum and does not exhibit any remarkable band/feature (Figure S45). A set of the kinetic traces ranging from 550 to 750 nm were analyzed by means of a global fit, including two-time constants, to describe the dynamics during the first nanoseconds after photoexcitation. Table S2 includes the resulting time constants for all the species studied. The fastest components (of the order of a few tens of picoseconds) were associated with electron transfer

processes from HOCO to LUCO of MOFs,⁷⁹ whereas the longer-lived components, which remained up to the nanosecond time scale, were assigned to a deep trap state.⁸⁰ Figure 7a shows for nitro-functionalized UiO-66 solids a comparison of the transients together with the average lifetimes calculated for each probe wavelength on the basis of the time constants derived from the global fit. The data reveal that the fastest relaxation dynamics is that of RuO_x@UiO-66(Zr/Ti)-NO₂ followed by an analogous mixed-metal UiO-66(Zr/Ti)-NO₂ parent sample, whereas monometallic UiO-66(Zr)-NO₂ exhibited longer-lived components. Similar conclusions can be drawn for amino-functionalized UiO-66 materials (Figure S44). In this regard, kinetic traces have been used as indicators to evaluate electron–hole separation efficiency of the photocatalysts. It is therefore proposed, by means of comparisons with previous ultrafast results from related MOFs,⁷⁹ that the faster the relaxation dynamics is, the higher is the charge-separation efficiency. In fact, the order of photocatalytic activity in our case agrees, to some extent, with the relaxation trace kinetics using ultrafast TAS measurements.

Long-lived trap states for UiO-66 photocatalysts were further investigated on longer time scales by the laser flash photolysis (LFP) technique at $\lambda_{\text{exc}} = 266$ nm. The spectra obtained for the different nitro- (Figure 7b and Figure S46) and amino- (Figure S47) functionalized UiO-66 photocatalysts in an Ar atmosphere on the nanosecond time scale were characterized by a continuous absorption band from 300 to 750 nm. Previous TAS studies by some of us using UiO-66(Zr)-X (X: NH₂ or NO₂) assigned these transient absorption bands to photogenerated electron and holes based on selective quenching experiments.^{51,54} Similar conclusions have been obtained in the present case using methanol as hole quencher for the series of amino-functionalized UiO-66 solids. Figure S48 shows that methanol quenches the region from 300 to 400 nm, resulting in a parallel increase of the transient signals around 600 nm, which indicates that hole deactivation enhances the yield of photogenerated electrons, an effect previously found in other related MOF-based photocatalysts.^{81,82} These results agree with those obtained from ultrafast TAS and demonstrate the photogeneration of charge separation species as electrons and holes. In line with the ultrafast results, LFP decay traces at 400 and 680 nm show that the faster the decay components are (see Table S2), the higher is the photocatalytic activity of all the studied RuO_x NPs supported UiO-66(Zr/Ti)-X (X: NH₂ or NO₂) in their series. In short, in terms of photocatalyst decay relaxation dynamics, both fs- and ns-TAS serve as

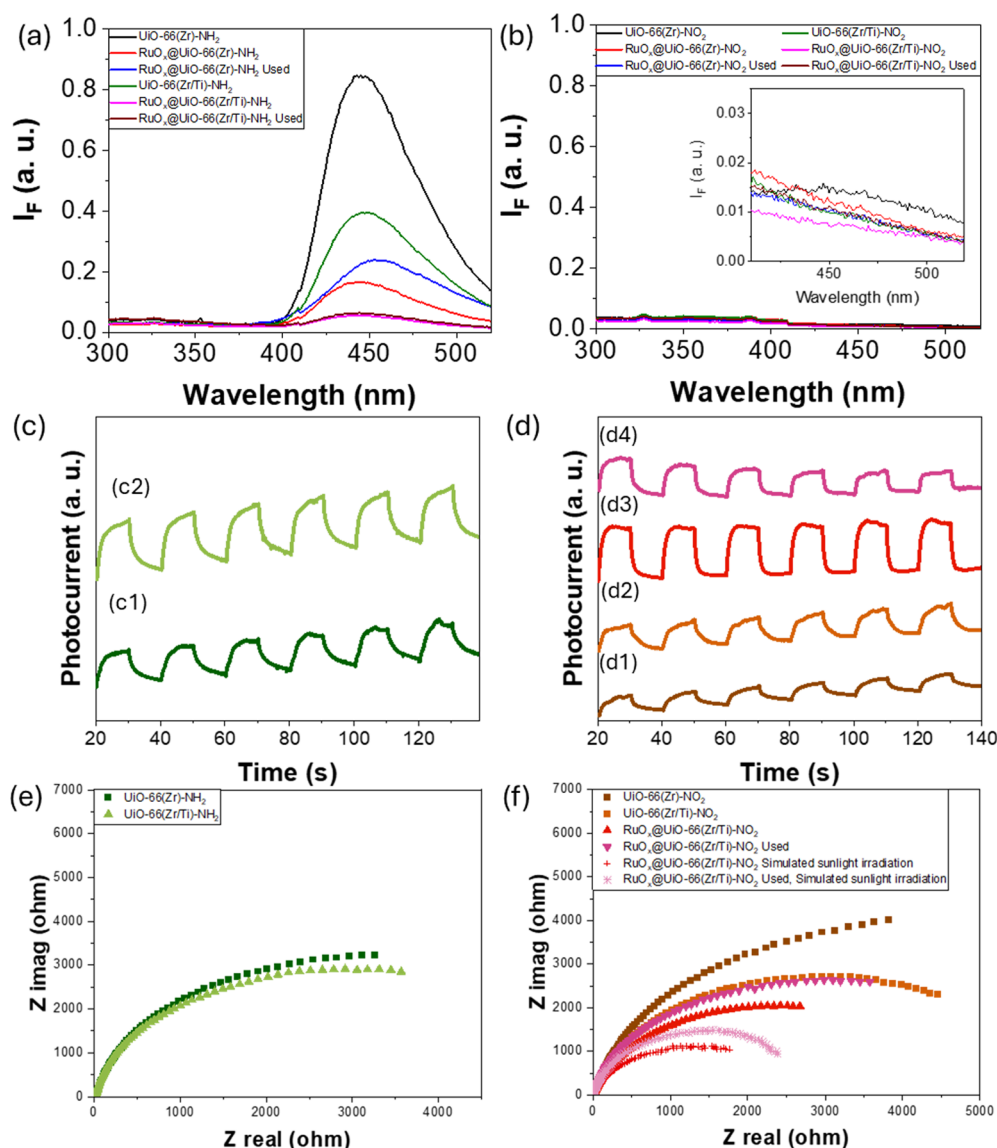


Figure 8. (a) PL measurements performed in acetonitrile MOF suspension having the same optical absorption (*ca.* 35 au) at 266 nm corresponding with the monochromatic excitation wavelength of the MOF organic. (b) Current intensity response of amino- (c) or nitro-based (d) UiO-66 solids. Nyquist plots of amino- (e) or nitro-based (f) UiO-66 solids under dark or simulated concentrated sunlight irradiation as indicated. Legend: (c1) UiO-66(Zr)-NH₂, (c2) UiO-66(Zr/Ti)-NH₂, (d1) UiO-66(Zr)-NO₂, (d2) UiO-66(Zr/Ti)-NO₂, (d3) RuO_x@UiO-66(Zr/Ti)-NO₂ fresh, and (d4) RuO_x@UiO-66(Zr/Ti)-NO₂ used.

indicators of charge separation efficiency and agree with the order observed in their photocatalytic activity.

To further evaluate the photoinduced charge separation efficiency of UiO-66 solids and their relationship with their photocatalytic activities, photocatalysts were characterized by PL spectroscopy and transient photocurrent and EIS measurements. PL spectroscopy is commonly used in heterogeneous photocatalysis, including MOFs, to evaluate the photoexcited charge transfer and recombination processes.^{83,84} Amino functionalized UiO-66 solids have a different degree of fluorescence, whereas negligible emission was found when using the nitro-functionalized solids. These results agree with some of our previous results showing that acetonitrile solutions of 2-aminoterephthalate emit much more on excitation at 266 nm than the analogous 2-nitroterephthalate acetonitrile solutions.⁵⁴ Figure 8a shows that the UiO-66(Zr/Ti)-NH₂ suspension has lower emissions than UiO-66(Zr)-NH₂, which agrees with similar studies that highlighted the higher efficiency

of photoinduced charge separation of mixed-metal UiO-66(Zr/Ti)-NH₂ solids, in which Ti(IV) atoms act as the electron mediator during the process.⁴⁸ Similar measurements using fresh or used RuO_x NPs supported UiO-66(Zr)-NH₂, and specially UiO-66(Zr/Ti)-NH₂ solids, produced considerably less fluorescence emission intensity. Regardless of the much lower fluorescence emission intensity observed when using nitro-functionalized UiO-66-based solids compared to amino ones, analogous conclusions about the fluorescence quenching in mixed-metal solids with or without fresh and used RuO_x with respect to the parent sample can be drawn (Figure 8b). These results indicate that the presence of RuO_x NPs in the UiO-66 solids reduces the recombination rate of photogenerated electron–hole pairs and thus increases the efficiency of photoinduced charge separation.

The transient photocurrent results using UiO-66 solids under several on/off illumination cycles are shown in Figure 8. For these measurements, UiO-based photocatalysts were

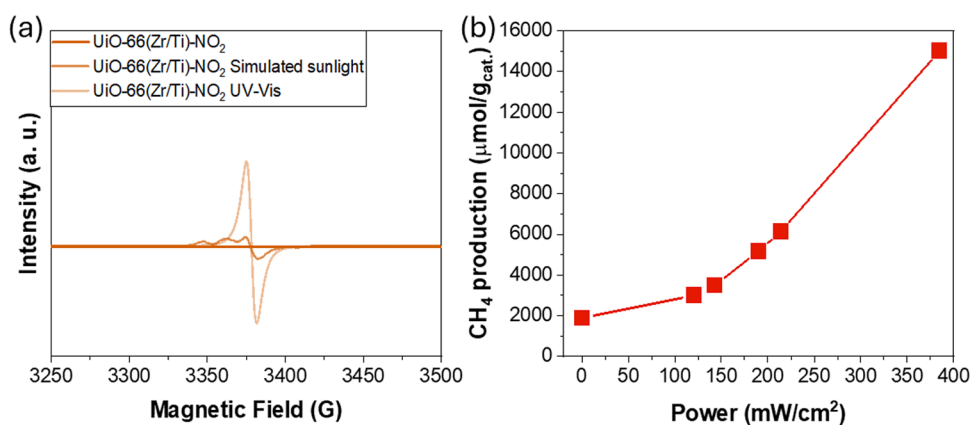


Figure 9. (a) EPR of solid UiO-66(Zr/Ti)-NO₂ after different irradiation conditions as indicated. (b) Influence of simulated light intensity into photocatalytic CH₄ formation.

supported on a carbon substrate electrode and used in a standard three-electrode electrochemical cell as a working electrode previously polarized at +0.9 V. The results show that mixed-metal UiO-66 solids have higher photocurrent intensities than monometallic ones (Figure 8). Analogous measurements using used and fresh RuO_x@UiO-66(Zr/Ti)-NO₂ photocatalysts found higher current intensities in simulated concentrated sunlight illumination and indicated an improvement in charge separation efficiency. An additional experiment using fresh RuO_x@UiO-66(Zr/Ti)-NO₂ in the presence of methanol gave a fivefold enhancement of current intensity (Figure S49). This was due to the oxidation of methanol in the photogenerated holes that partially avoided electron recombination so that a higher current intensity was measured than in the experiment with pure acetonitrile as solvent.

PL and transient photocurrent conclusions were complemented by EIS measurements (Figure 8). The smallest Nyquist arc radii were obtained from the most active samples of the series with the lowest charge transfer resistance. PL, transient photocurrent, and EIS measurements showed that titanium ions in the metal nodes of UiO-66(Zr/Ti) and/or RuO_x@UiO-66 solids acted as electron mediators during the photoinduced electron transfer from the organic ligand to the metal node and increased the process efficiency.^{48,84}

Previous studies reported the use of solid-state ESR spectroscopy to characterize the formation of photoactive reductive sites in MOFs like UiO-66(Zr)-NH₂^{54,58} or MIL-125(Ti)-NH₂. For example, it has been reported that irradiation of UiO-66(Zr)-NH₂ results in photoinduced charge separation from the organic ligand to the metal node and the transformation of Zr(IV) species into Zr(III) species while the holes are located in the organic ligand.^{54,58,85} Other studies have proposed that the irradiation of mixed-metal UiO-66(Zr/Ti)-NH₂ produces an LMCT mechanism with the initial reduction of Ti(IV) to Ti(III) in Ti(III)-O-Zr(IV) metal nodes, which are later transformed into Ti(IV)-O-Zr(III).⁴⁸ These studies highlight the role of Ti(IV) species in mixed-metal UiO-66 solids as electron mediators from excited organic ligands that favor charge separation. In the present study, solid-state ESR experiments were carried out using UiO-66(Zr)-X (X: NH₂ or NO₂) and the analogous mixed-metals UiO-66(Zr/Ti)-X (X: NH₂ or NO₂) (Figure 9 and Figure S50). Control solid-state ESR experiments in dark conditions revealed the presence of some paramagnetic signals in amino-functionalized UiO-66 associated with the presence of

Zr(III) species that, however, are absent in analogous nitro solids, in agreement with previous related studies.⁵⁴ Irradiation of mono- or bimetallic UiO-66 solids functionalized with either amino or nitro groups in all cases produced the formation of an ESR band with *g* value of 2.004, characteristic of the Zr(III) species. These experiments indicate the occurrence of LMCT mechanisms in MOFs, whereas the absence of ESR Ti(III) signals could be associated with the previously proposed fast kinetics of metal electron transfer from Ti(III) as electron mediator to geminal Zr(IV).⁴⁸

Based on previous studies and due to the use of RuO_x NPs as cocatalysts during photocatalytic CO₂ reduction, the occurrence of a photothermal pathway can be hypothesized in which light energy is transformed into heat energy.^{75–77} An indirect experiment to determine this possible pathway was conducted by evaluating photocatalytic CO₂ methanation as a function of the simulated sunlight intensity. Figure 9 shows that photocatalytic methane production increases linearly as a function of irradiance intensity up to about 125 mW/cm², and then an exponential relationship can be seen. These results are interpreted as the occurrence of a photothermal reaction pathway, especially at high irradiance intensities, in which light irradiation is transformed into local heat in RuO_x NPs, promoting CO₂ hydrogenation to CH₄.

The measurement of catalyst temperature during the photothermal reaction is of great importance to understand the thermal- and nonthermal contributions of the whole process.⁸⁶ To address this challenging measurement, several techniques have been reported like direct measurement with a thermocouple or noncontact techniques with infrared sensors or thermal cameras.⁸⁶ Another common method to assess catalyst local heating is based on the use of supported inorganic quantum dots (QDs) as temperature sensors with optical readout.^{26,87} Specifically, the measurement of PL emission decrease of supported QDs on a photocatalyst is a function of the local temperature.^{26,43} In this work, commercially available CdSe-ZnS QDs were employed as local nanothermometers. A series of PL experiments upon CdSe-ZnS QDs excitation at 450 nm were performed at temperatures from 200 to 280 °C under dark or upon simulated sunlight irradiation intensities from 85 to 385 mW/cm². Figure S51 shows that the characteristic PL emission band of CdSe-ZnS QDs centered about 540 nm gradually decreases as the temperature increases. These experiments confirmed the possibility of using these CdSe-ZnS QDs as local nano-

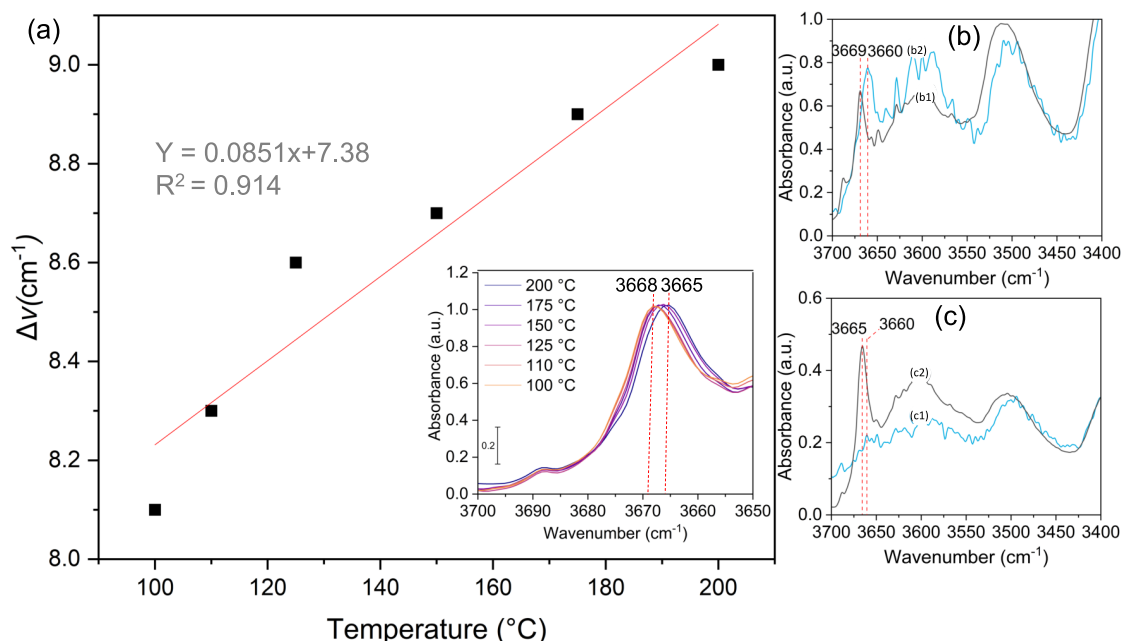


Figure 10. (a) Evolution of the structural band shift as a function of temperature (inset: direct surface FTIR spectra of $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ in the $3700\text{--}3650\text{ cm}^{-1}$ region at different temperatures in the dark). (b, c) FTIR spectra in the same region (1) in the dark and (2) under irradiation at 30 and 200 °C, respectively. Spectra collected under continuous flow of Ar ($20\text{ cm}^3/\text{min}$).

thermometers, in agreement with previous reports.^{26,43} Additionally, the PL emission intensity of CdSe-ZnS QDs recorded at 200 °C also decreased upon irradiation, the highest the irradiation intensity the highest the PL quenching, a fact associated with the local heating of CdSe-ZnS QDs upon irradiation. Analogous PL results were obtained in the case of used $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ photocatalyst supported CdSe/ZnS QDs deposited on a quartz holder as a function of either the temperature or the simulated sunlight irradiation at different irradiances. It should be noted that during these PL experiments, negligible temperature changes of the sample upon different irradiations were measured using an infrared thermometer. Therefore, it is likely to propose that the observed PL quenching upon irradiation might be associated with a photocatalyst local heating (*ca.* to about 220 or 280 °C as a function of the irradiance; Figure S52) due to irradiation. Overall, these PL results together with those ones shown in Figure 9 about the influence of simulated light intensity into photocatalytic CH_4 formation would agree with the occurrence of a photothermal reaction pathway during CO_2 reduction.

Further investigation of the photothermal behavior was conducted by monitoring the IR band shift the structural bands using operando FTIR experiments under different temperatures given the fact that as temperature increases, the molecular vibration of the different species increases, resulting in a shift in IR bands.^{88,89} Results confirm this behavior with $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ showing a structural band shift from 3668 to 3664 cm^{-1} (assigned to OH vibration) as temperature increased from 100 to 200 °C under dark conditions (inset of Figure 10a). This effect was then investigated for the reaction under irradiation at room temperature. Interestingly, a significant band shift from 3369 to 3360 cm^{-1} (Figure 10b) is observed indicating a potential localized temperature increase (estimated at around 145 °C). However, at an elevated temperature (200 °C), this effect was diminished, whereby a lower band shift is observed (Figure

10c). This result is consistent with that of the PL quenching with QDs.

Overall, RuO_x NPs supported $\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ generally acts as a multifunctional photocatalyst during CO_2 methanation under simulated concentrated sunlight irradiation (Figure 11). During the photochemical pathway irradiation of

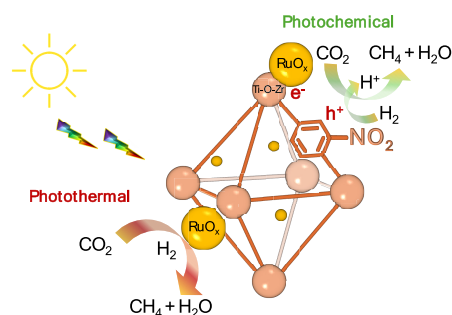


Figure 11. Proposed reaction mechanism during CO_2 methanation using $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ as multifunctional photocatalyst.

the photocatalyst, we consider that a photoinduced electron transfer from the organic ligand to the metal-oxo cluster takes place. These electrons can be further transferred to RuO_x NPs, where CO_2 methanation occurs. Irradiation can also promote the heating of RuO_x NP and CO_2 hydrogenation to methane.

3.3.2. Evaluation of Photocatalytic CO_2 Hydrogenation to CH_4 . The previous photocatalytic results using UiO-66-based materials have shown a selective CO_2 hydrogenation to CH_4 . These results agree with analogous studies reporting that the use of supported RuO_x NPs facilitates chemisorption of CO_2 and their reaction intermediates and promote the (photo)-catalytic hydrogenation to methane.^{90–92} To shed some light on the CO_2 and CO adsorption capacity over $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ topic, CO_2 and CO adsorption experiments were conducted under continuous flow of CO_2/Ar and CO/Ar

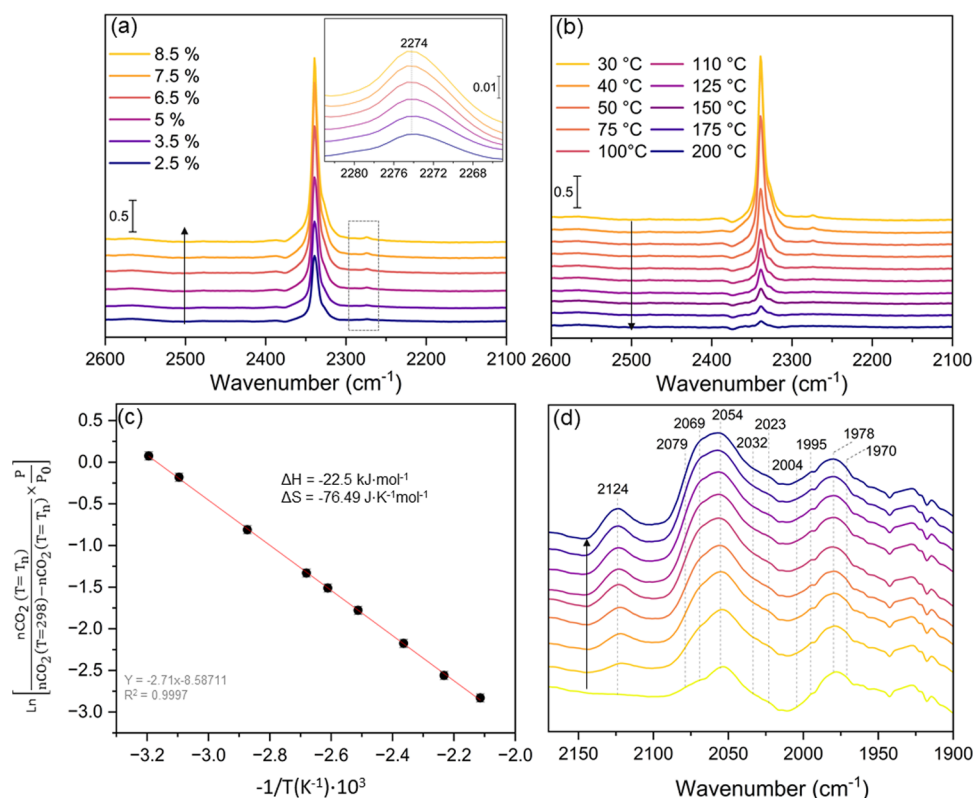


Figure 12. (a, b) FTIR spectra of chemisorbed CO₂ on RuO_x@UiO-66(Zr/Ti)-NO₂ versus different concentrations of CO₂ in argon and temperatures, respectively (total flow rate = 20 cm³·min⁻¹); (c) the corresponding enthalpy and the entropy of the CO₂ chemisorption; and (d) evolution of FTIR spectra of adsorbed CO on RuO_x@UiO-66(Zr/Ti)-NO₂ in 2150–1900 cm⁻¹.

under operando conditions, and the results were analyzed through FTIR.^{93,94} Initially, different concentrations of CO₂ were introduced in Ar with a total flow rate of 20 cm³·min⁻¹. It is witnessed that as the concentration of CO₂ increases, the band centered at 2238 cm⁻¹ characteristic of chemisorbed CO₂ increases in a linear way, as illustrated in Figure 12a. The results are presented after subtraction of gaseous CO₂ phase. Direct spectra can be found in the SI (Figure S53a). Upon reaching saturation, CO₂ adsorption was investigated as a function of the temperature (as depicted in Figure 12b). These results demonstrated an exponential decrease in chemisorbed CO₂ concentration as the temperature increases, until reaching 30 °C. Subsequently, the enthalpy and entropy of this reaction were calculated based on the linear relationship of $\ln \left[\frac{n_{\text{CO}_2}(T=298)}{n_{\text{CO}_2}(T=T_n)} \times \frac{P}{P_0} \right]$ (where n_{CO_2} represents the number of moles of chemisorbed CO₂, T_n is the temperature reached at each point, and P/P_0 is the relative pressure of CO₂ in Ar) as a function of the inverse of temperature ($-1/T$), as shown in Figure 12c. The enthalpy of the reaction was determined from the slope of the line and equal to -22.5 kJ/mol , indicating relatively weak and reversible adsorption of CO₂ on the catalyst surface. The investigation of CO adsorption on supported ruthenium catalysts holds significance not only for understanding the mechanism of CO₂ methanation reaction (considering that CO is one of the potential intermediates of this reaction) but also for the characterization of their surface properties. CO serves as a prominent probe molecule, unveiling both the oxidation state and coordination environment of the sites to which it binds. Figure 12d shows the evolution of the FTIR

spectra of the RuO_x@UiO-66(Zr/Ti)-NO₂ in the CO vibration spectral region (2200–1800 cm⁻¹) upon the introduction of 0.05% CO in Ar to the sample preactivated under hydrogen at 200 °C. The results are subtracted from the spectrum after activation at room temperature, and the direct spectra can be found in the Figure S53b. Different bands appeared on the surface; however, their assignment to specific adsorption sites is not straightforward, as witnessed by the different interpretations found in the literature. This variability likely arises from multiple factors influencing exact band positions, such as the coverage of CO, as well as the oxidation state of the adsorbant. According to literature findings, carbonyl species can predominantly be categorized into two distinct surface complexes: the spectral peaks at 2124 cm⁻¹, coupled with a component at 2055 cm⁻¹, are attributed to the asymmetric and symmetric stretching vibrations of a Ru³⁺(CO)₂ species on the proximity of ZrO₂.⁹⁵ Meanwhile, the spectral peaks at 2070 and 2004 cm⁻¹ are associated with those of Ru²⁺(CO)₂ species.⁸⁹ Furthermore, peaks at lower wavenumbers (1995, 1987, and 1955 cm⁻¹) may be attributed to monocarbonyls adsorbed on less oxidized Ru^{δ+} supported on TiO₂. Furthermore, a less intense peak at 2023 cm⁻¹ may be attributed to CO linearly bound to metallic Ru⁰. The approximative assignments of the spectral bands are summarized in Table S3.

The performance of the most active RuO_x@UiO-66(Zr/Ti)-NO₂ sample during photocatalytic CO₂ hydrogenation to CH₄ was further investigated through operando FTIR experiments where both the gas phase products and the surface of the catalyst are analyzed simultaneously in real time under similar irradiation conditions used previously in batch.^{96–98} The setup

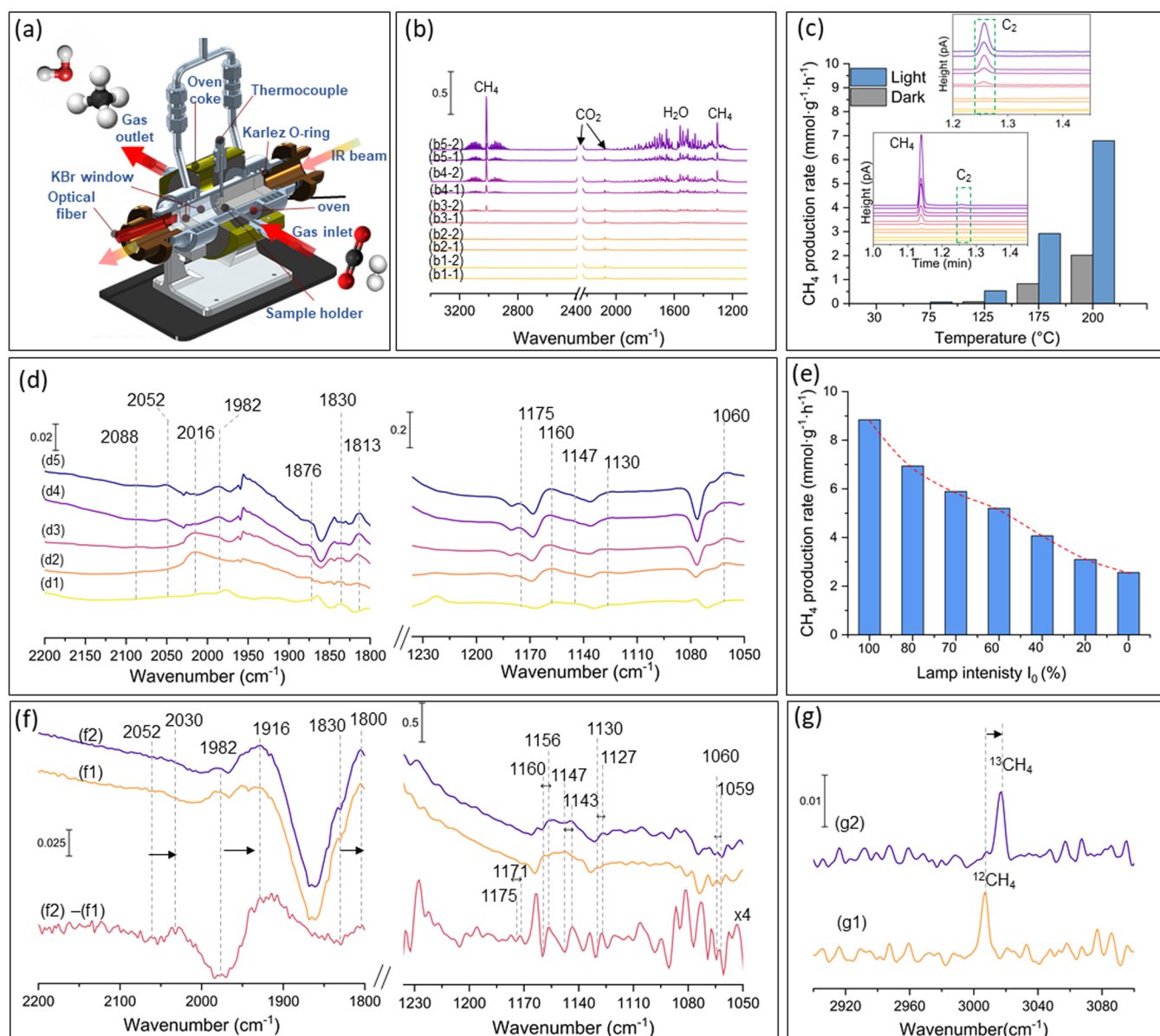


Figure 13. (a) Sandwich IR reactor-cell used for studying the CO₂ methanation reaction under visible light in continuous flow. (b) The FTIR spectra of the reaction gas phase: (b1) 30, (b2) 75, (b3) 125, (b4) 175, and (b5) 200 °C (-1) in the dark and (-2) after irradiation at steady state. (c) Activity of RuO_x@UiO-66(Zr/Ti)-NO₂ as a function of temperature in the dark and under visible light irradiation (inset: gas chromatograms of the reaction gas phase under the same conditions). (d) Operando FTIR spectra of RuO_x@UiO-66(Zr/Ti)-NO₂ versus temperature: (d1) 30, (d2) 75, (d3) 125, (d4) 175, and (d5) 200 °C in the 2200–1800 and the 1200–1000 cm⁻¹ vibrational regions. (e) Activity of RuO_x@UiO-66(Zr/Ti)-NO₂ as a function of lamp intensity. (f) FTIR spectra of the catalyst during the photoassisted methanation at 200 °C of (1) ¹³CO₂ and (2) ¹²CO₂; the corresponding subtracted spectrum (¹³CO₂ – ¹²CO₂) presented in (d3) (intensity was multiplied by 4 for clarity). (g) FTIR gas phase spectra of gaseous methane produced during the photoassisted methanation of (1) ¹²CO₂ and (2) ¹³CO₂ at 200 °C. The arrow corresponds to the shift of the IR bands due to the isotopic exchange from ¹²CO₂ to ¹³CO₂. The assignments of the different IR bands are summarized in Tables S3 and S4.

is equipped with an online mass spectrometer (MS) and gas chromatography (GC) whereby online injections are taken throughout the reaction. A “Sandwich” cell reactor (Figure 13a) was used to carry out these experiments where the catalyst is fixed in the cell as a self-supported pallet (20 mg). The sample was first activated under hydrogen at 200 °C, and then its activity for the CO₂ methanation was assessed with a molar ratio of 4:1 of H₂ to CO₂ with a total flow rate of 10 cm³·min⁻¹. The photothermal CO₂ methanation activity of RuO_x@UiO-66(Zr/Ti)-NO₂ was tested under different temperatures (Figure 13b,c). No methane production was detected at 30 °C either in darkness or under visible light

irradiation, as evidenced by the analysis of the gas phase at the steady state. However, upon reaching 75 °C, methane production increased with rising temperature in the absence of light. Interestingly, under irradiation, methane production exhibited a significant increase with increasing temperature, reaching 8 mmol·g⁻¹·h⁻¹ at 200 °C, with a selectivity of 98.3%. This observation was further confirmed by FTIR analysis, which revealed only CH₄ and H₂O as gas phase products (Figure 13b). Complementary results of the GC analysis showed, in addition to methane, the production of ethane (under the detection limit of our FTIR-gas analysis) as a side product with a selectivity of 1.7% (inset of Figure 13c).

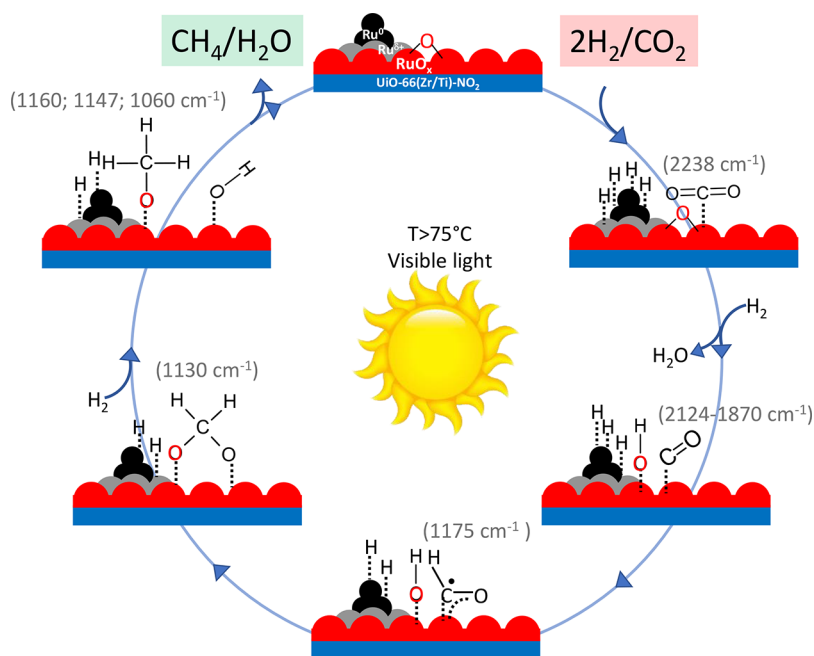


Figure 14. Proposed mechanism of the photoassisted CO_2 methanation over $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ based on the assignment of the characteristic FTIR bands of the various species.

Subsequently, an investigation into the impact of lamp intensity on the activity of $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$ was carried out at 200 °C, as illustrated in Figure 13e. The sample's activity decreased in quasi-linear manner from 8.7 to 3.5 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ as the relative intensity of the lamp decreased from 100 to 20% I_0 . No significant deactivation was observed, in agreement with the previous experiments that were conducted in batch conditions at different simulated sunlight irradiation intensities. The decline in the sample's activity with decreasing lamp intensity suggests a diminished prominence of plasmonic effects during the reaction under irradiation. This indicates that the catalytic behavior may be governed by factors beyond predominant plasmonic-mediated mechanisms.

In an attempt to gain more information on the underlying mechanism of the CO_2 hydrogenation over $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$, the surface of the catalyst was simultaneously monitored by FTIR during the reaction. The FTIR spectra of the surface, at steady state, between 30 and 200 °C are shown in Figure 13d. Results are subtracted from the spectrum at 30 °C of the preactivated sample. It is essential to note that the spectral regions corresponding to the stretching vibration of formates and carbonates, specifically between 1600 and 1300 cm^{-1} , are saturated. Therefore, for assigning the different possible reaction intermediates, both the CO vibrational region and the unobstructed region between 1200 and 1000 cm^{-1} are taken into consideration. Different bands emerged as temperature increased in the CO region mainly at 2088 and 1985 cm^{-1} possibly attributed to adsorbed CO on $\text{Ru}^{\delta+}$ on the proximity of TiO_2 .⁸⁹ Furthermore, a band emerged as temperature increased from 30 to 75 °C at 2016 cm^{-1} , after which it diminished. This decrease was accompanied by the start of the methane production at 75 °C (Figure 13b curve b4). This band could be attributed to CO linearly adsorbed on Ru^0 . These results indicate that the formation of CO on the surface is promoted at lower temperatures even if no methane is produced yet. CO in the gas phase was not detected at high temperatures, which emphasizes its key role as an intermediate

in the CO_2 methanation reaction over $\text{RuO}_x@\text{UiO-66}(\text{Zr/Ti})\text{-NO}_2$. At higher temperatures, the formation of formyl as an intermediate was suggested by the presence of the band at 1175 cm^{-1} .⁹⁹ Furthermore, various bands corresponding to methoxy species are observed in the spectra at 1160 (on-top) and 1060 (doubly bridging) cm^{-1} owing to the stretching vibrations of methoxys.¹⁰⁰ Also, a band at 1130 cm^{-1} elevated as temperature increased, probably attributed to dioxymethylene adsorbed on the surface.¹⁰¹ It is important to mention that increasing the temperature causes a shift in the vibrational bands of species present on the surface,⁸⁸ justifying the negative signals on the subtracted spectra.

To confirm the involvement of the various species in the reaction mechanism and their intermediates role, a steady-state isotopic transient kinetic analysis (SSITKA) experiment using operando FTIR spectroscopy was performed at 200 °C.¹⁰² It corresponds to replacing $^{12}\text{CO}_2$ by its isotope $^{13}\text{CO}_2$ at steady state under the same reaction conditions. The isotopic transient leads to shift of the FTIR bands of the surface intermediates. Additionally, this approach ensures that any observed shift would solely result from isotopic exchange between $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ and not due to the change of temperature and structural band's shift. However, because of the fact that pure $^{13}\text{CO}_2$ is very expensive, this experiment was carried out under diluted conditions (1% of $^{12}\text{CO}_2$ in argon and then exchanged to 1% of $^{13}\text{CO}_2$ in argon). Interestingly, $^{13}\text{CH}_4$ was produced selectively with $^{13}\text{CO}_2$ with a similar quantity to that produced with $^{12}\text{CO}_2$ under similar conditions (Figure 13g). This was accompanied by the shift (3 or 4 cm^{-1} ; Table S4) in FTIR bands of different species previously attributed to CO, formyl, methoxy, and dioxymethylene with $^{13}\text{CO}_2$, as depicted in Figure 13f. Therefore, these observations confirm the role of these species as reaction intermediates. It should be noted that because of the overlap with the CO vibration, it was difficult to distinguish the band related to the hydride bond formed by hydrogen dissociation on reduced Ru.

Based on the spectral investigations mentioned above, an overall mechanism is proposed for the reaction unfolding as illustrated in Figure 14. Initially, CO₂ is adsorbed on the surface, primarily on Ru species, accompanied by a hydride formation of reduced Ru. Subsequently, CO is generated as the primary intermediate of CO₂ reduction, which exhibits strong surface adsorption. This is evident from the absence of CO as final product in the gas phase, as confirmed by FTIR and GC analyses (Figure 13b,c). As temperature increases, the photoassisted reduction of CO to formyl is promoted, followed by its conversion to dioxymethylene through interaction with surface oxygen. Then, the photoassisted reduction of dioxymethylene produces methoxy as the final intermediate species before generating methane and water as final products through further reduction. This mechanism emphasizes the dual role of RuO_x and reduced Ru in the production of methane from CO₂ and H₂.

4. CONCLUSIONS

This study describes the development of multifunctional and photocatalytically active UiO-66 solids supported RuO_x NPs (2 ± 0.1 nm) for CO₂ methanation at 200 °C under simulated concentrated sunlight irradiation. The photocatalytic activity of the samples followed the order UiO-66(Zr/Ti)-NO₂ > UiO-66(Zr/Ti)-NH₂ ~ UiO-66(Zr)-NO₂ > UiO-66(Zr)-NH₂. In contrast to most reports involving UiO-66 photocatalysts based on the use of the 2-aminoterephthalate ligand, the present study highlights the importance of using 2-nitroterephthalate ligands to achieve high activity with Zr(IV) or mixed-metal Zr(IV)/Ti(IV) nodes within UiO-66-based materials and associated with the unique energy band level diagram of these solids. It should be noted that UiO-66(Zr/Ti)-NO₂ is a reusable photocatalyst that exhibits record activity (5.03 mmol g⁻¹ after 22 h; AQY at 350, 400, and 600 nm of 1.67, 0.25, and 0.01%, respectively) compared to previous analogous reports on MOF-based materials. Based on the results of several spectroscopic, electrochemical, and photocatalytic experiments, we consider that RuO_x@UiO-66(Zr/Ti)-NO₂ operates in a dual photochemical and photothermal reaction pathway. The photocatalytic CO₂ hydrogenation pathway was further investigated in flow condition using operando FTIR spectroscopy. The results are in very good agreement with those obtained under batch conditions. Based on the surface analysis and SSITKA experiment, a mechanism involving CO, formyl, dioxomethane, and methoxy, as intermediates, has been illustrated. In summary, we propose an innovative combination of nitro functionalized UiO-66 solids with mixed-metal Zr(IV)/Ti(IV) nodes and supported RuO_x NPs as cocatalyst to progress toward solar-driven photocatalytic CO₂ methanation. The authors consider that this work will open new possibilities for the development of multifunctional MOFs as solar-driven photocatalysts for selective CO₂ transformations.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c00266>.

Synthesis of the MOF-based materials; characterization techniques; photocatalytic activity; SEM and SEM-EDX mapping images; TEM images; XPS spectra; isothermal N₂ adsorption graphs; TGA analyses; UV-vis diffuse

reflectance spectra; valence band XPS spectra; PXRD; mass spectrum of ¹⁷CH₄; femtosecond transient absorption spectra and decay traces; LFP spectra and decay traces; transient photocurrent plot; EPR spectra; direct spectra of chemisorbed CO₂ and CO over RuO_x@UiO-66(Zr/Ti)-NO₂; photocatalytic CO₂ methanation by H₂ using MOF-based photocatalysts reported in the literature (Table S1); global fit analysis (Table S2); different vibrational modes of adsorbed CO over RuO_x@UiO-66(Zr/Ti)-NO₂ (Table S3); and vibrational modes of different adsorbed species over RuO_x@UiO-66(Zr/Ti)-NO₂ during the CO₂ methanation reaction (Table S4) (PDF)

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Notes

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REFERENCES

- (1) Bosa, K.; Gupta, J. Stranded assets and stranded resources: Implications for climate change mitigation and global sustainable development. *Energy Res. Soc. Sci.* **2019**, *56*, 101215.
- (2) Paraschiv, S.; Paraschiv, L. S. Trends of carbon dioxide (CO₂) emissions from fossil fuels combustion (coal, gas and oil) in the EU member states from 1960 to 2018. *Energy Rep.* **2020**, *6*, 237–242.
- (3) Østergaard, P. A.; Duic, N.; Noorollahi, Y.; Mikulcic, H.; Kalogirou, S. Sustainable development using renewable energy technology. *Renew. Energy* **2020**, *146*, 2430–2437.
- (4) Sherwood, J. The significance of biomass in a circular economy. *Bioresour. Technol.* **2020**, *300*, No. 122755.
- (5) Radovanović, M.; Filipović, S.; Vukadinović, S.; Trbojević, M.; Podbregar, I. Decarbonisation of eastern European economies: monitoring, economic, social and security concerns. *Energy Sustain. Soc.* **2022**, *12*, 16.
- (6) de Kleijne, K.; Hanssen, S. V.; van Dinteren, L.; Huijbregts, M. A. J.; van Zelm, R.; de Coninck, H. Limits to Paris compatibility of CO₂ capture and utilization. *One Earth* **2022**, *5*, 168–185.
- (7) Mac Dowell, N.; Fennell, P. S.; Shah, N.; Maitland, G. C. The role of CO₂ capture and utilization in mitigating climate change. *Nat. Clim. Change* **2017**, *7*, 243–249.
- (8) Mikkelsen, M.; Jørgensen, M.; Krebs, F. C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81.
- (9) Ding, M.; Flaig, R. W.; Jiang, H.-L.; Yaghi, O. M. Carbon capture and conversion using metal–organic frameworks and MOF-based materials. *Chem. Soc. Rev.* **2019**, *48*, 2783–2828.
- (10) Zhang, Z.; Pan, S.-Y.; Li, H.; Cai, J.; Olabi, A. G.; Anthony, E. J.; Manovic, V. Recent advances in carbon dioxide utilization. *Renewable Sustainable Energy Rev.* **2020**, *125*, No. 109799.
- (11) Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. Sustainable conversion of carbon dioxide: An integrated review of catalysis and life cycle assessment. *Chem. Rev.* **2018**, *118*, 434–504.
- (12) Dhakshinamoorthy, A.; Navalón, S.; Primo, A.; García, H. Selective gas-phase hydrogenation of CO₂ to methanol catalysed by metal-organic frameworks. *Angew. Chem., Int. Ed.* **2023**, *136*, e202311241.
- (13) Bellabarba, R.; Johnston, P.; Moss, S.; Sievers, C.; Subramaniam, B.; Tway, C.; Wang, Z.; Zhu, H. Net zero transition: possible implications for catalysis. *ACS Catal.* **2023**, *13*, 7917–7928.
- (14) De, S.; Dokania, A.; Ramirez, A.; Gascon, J. Advances in the design of heterogeneous catalysts and thermocatalytic processes for CO₂ utilization. *ACS Catal.* **2020**, *10*, 14147–14185.
- (15) Lin, H.; Luo, S.; Zhang, H.; Ye, J. Toward solar-driven carbon recycling. *Joule* **2022**, *6*, 294–314.
- (16) Lewis, N. S. Research opportunities to advance solar energy utilization. *Science* **2016**, *351*, 1920.
- (17) Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729–15735.
- (18) Ciocarlan, R.-G.; Blommaerts, N.; Lenaerts, S.; Cool, P.; Verbruggen, S. W. Recent trends in plasmon-assisted photocatalytic CO₂ reduction. *ChemSusChem* **2023**, *16*, 202201647.
- (19) Wang, Q.; Domen, K. Particulate photocatalysts for light-driven water splitting: Mechanisms, challenges, and design strategies. *Chem. Rev.* **2020**, *120*, 919–985.
- (20) Halmann, M. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature* **1978**, *275*, 115–116.
- (21) Thampi, K. R.; Kiwi, J.; Graetzel, M. Methanation and photo-methanation of carbondioxide at room-temperature and atmospheric pressure. *Nature* **1987**, *327*, 506–508.
- (22) Chen, D.; Zhang, X.; Lee, A. F. Synthetic strategies to nanostructured photocatalysts for CO₂ reduction to solar fuels and chemicals. *J. Mater. Chem. A* **2015**, *3*, 14487–14516.
- (23) Li, X.; Yu, J.; Jaroniec, M.; Chen, X. Cocatalysts for selective photoreduction of CO₂ into solar fuels. *Chem. Rev.* **2019**, *119*, 3962–4179.
- (24) Ulmer, U.; Dingle, T.; Duchesne, P. N.; Morris, R. H.; Tavasoli, A.; Wood, T.; Ozin, G. A. Fundamentals and applications of photocatalytic CO₂ methanation. *Nat. Commun.* **2019**, *10*, 3169.
- (25) Mateo, D.; Albero, J.; García, H. Titanium-perovskite-supported RuO₂ nanoparticles for photocatalytic CO₂ methanation. *Joule* **2019**, *3*, 1949–1962.
- (26) Mateo, D.; Albero, J.; García, H. Photoassisted methanation using Cu₂O nanoparticles supported on graphene as a photocatalyst. *Energy Environ. Sci.* **2017**, *10*, 2392–2400.
- (27) Mateo, D.; Albero, J.; García, H. Graphene supported NiO/Ni nanoparticles as efficient photocatalyst for gas phase CO₂ reduction with hydrogen. *Appl. Catal. B-Environ.* **2018**, *224*, 563–571.
- (28) Barrio, J.; Mateo, D.; Albero, J.; García, H.; Shalom, M. A Heterogeneous Carbon Nitride–Nickel Photocatalyst for Efficient Low-Temperature CO₂ Methanation. *Adv. Energy Mater.* **2019**, *9*, 1902738.
- (29) Ali, F. M.; Ghuman, K. K.; O'Brien, P. G.; Hmadeh, M.; Sandhel, A.; Perovic, C. D. D.; Veer Singh, C.; Mims, C. A.; Ozin, G. A. Highly efficient ambient temperature CO₂ photomethanation catalyzed by nanostructured RuO₂ on silicon photonic crystal support. *Adv. Energy Mater.* **2018**, *8*, 1702277.
- (30) Albero, J.; Peng, Y.; García, H. Photocatalytic CO₂ reduction to C₂₊ products. *ACS Catal.* **2020**, *10*, 5734–5749.
- (31) Navalón, S.; Dhakshinamoorthy, A.; Álvaro, M.; Ferrer, B.; García, H. Metal–organic frameworks as photocatalysts for solar-driven overall water splitting. *Chem. Rev.* **2023**, *123*, 445–490.
- (32) Younas, M.; Loong Kong, L. L.; Bashir, M. J. K.; Nadeem, H.; Shehzad, A.; Sethupathi, S. Recent advancements, fundamental challenges, and opportunities in catalytic methanation of CO₂. *Energy Fuels* **2016**, *30*, 8815–8831.
- (33) Walspurger, S.; Haije, W. G.; Louis, B. CO₂ reduction to substitute natural gas: Toward a global low carbon energy system. *Isr. J. Chem.* **2014**, *54*, 1432–1442.
- (34) Khan, S.; Dai, X.; Ali, T.; Mahmood, S.; ul Haq, M.; Riaz, M. S.; Hu, Y. Recent advances on photo-thermo-catalysis for carbon dioxide methanation. *Int. J. Hydrog. Energy* **2022**, *48*, 24756–24787.
- (35) Zhao, J.; Liu, J.; Li, Z.; Wang, K.; Shi, R.; Wang, P.; Wang, Q.; Waterhouse, G. I. N.; Wen, X.; Zhang, T. Ruthenium-cobalt single atom alloy for CO photo-hydrogenation to liquid fuels at ambient pressures. *Nat. Commun.* **2023**, *14*, 1909.
- (36) Cabrero-Antonino, M.; Remiro-Buenamañana, S.; Souto, M.; García-Valdivia, A. A.; Choquesillo-Lazarte, D.; Navalón, S.; Rodríguez-Diéguez, A.; Mínguez-Espallargas, G.; García, H. Design of cost-efficient and photocatalytically active Zn-based MOFs decorated with Cu₂O nanoparticles for CO₂ methanation. *Chem. Commun.* **2019**, *55*, 10932–10935.
- (37) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A chromium terephthalate-based solid

with unusually large pore volumes and surface area. *Science* **2005**, *309*, 2040–2042.

(38) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444.

(39) Kitagawa, S.; Kitaura, R.; Noro, S.-I. Functional porous coordination polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.

(40) Dhakshinamoorthy, A.; Asiri, A. M.; García, H. Metal-organic framework (MOF) compounds: Photocatalysts for redox reactions and solar fuel production. *Angew. Chem., Int. Ed.* **2016**, *55*, 5414–5445.

(41) Li, R.; Zhang, W.; Zhou, K. Metal–Organic-Framework-Based Catalysts for Photoreduction of CO₂. *Adv. Mater.* **2018**, *30*, 1705512.

(42) Kolobov, N.; Goesten, M. G.; Gascon, J. Metal–organic frameworks: Molecules or semiconductors in photocatalysis? *Angew. Chem., Int. Ed.* **2021**, *60*, 26038–26052.

(43) Wang, S.; Cabrero-Antonino, M.; Navalón, S.; Chen-chen Cao, C.-c.; Tissot, A.; Dovgaliuk, I.; Marrot, J.; Martineau-Corcós, C.; Yu, L.; Wang, H.; et al. A robust titanium isophthalate metal-organic framework for visible-light photocatalytic CO₂ methanation. *Chem.* **2020**, *6*, 3409–3427.

(44) Cabrero-Antonino, M.; Ferrer, B.; Baldoví, H. G.; Navalón, S. Toward solar-driven photocatalytic CO₂ methanation under continuous flow operation using benchmark MIL-125(Ti)-NH₂ supported ruthenium nanoparticles. *Chem. Eng. J.* **2022**, *445*, No. 136426.

(45) Liu, H.; Cheng, M.; Liu, Y.; Zhang, G.; Li, L.; Du, L.; Li, B.; Xiao, S.; Wang, G.; Yang, X. Modified UiO-66 as photocatalysts for boosting the carbon-neutral energy cycle and solving environmental remediation issues. *Coord. Chem. Rev.* **2022**, *458*, No. 214428.

(46) Dufлот, M.; Marchal, C.; Caps, V.; Artero, V.; Christoforidis, K.; Keller, V. Optimization of NH₂-UiO-66/TiO₂/Au composites for enhanced gas-phase CO₂ photocatalytic reduction into CH₄. *Catal. Today* **2023**, *413–415*, No. 114018.

(47) Melillo, A.; García-Aboal, R.; Navalón, S.; Atienzar, P.; Ferrer, B.; Alvaro, M.; García, H. Photoactive Zr and Ti metal-organic-frameworks for solid-state solar cells. *ChemPhysChem* **2021**, *22*, 842–848.

(48) Santiago-Portillo, A.; Baldoví, H. G.; Fernandez, M. T. G.; Navalón, S.; Atienzar, P.; Ferrer, B.; Alvaro, M.; García, H.; Li, Z. Ti as Mediator in the Photoinduced Electron Transfer of Mixed-Metal NH₂-UiO-66(Zr/Ti): Transient Absorption Spectroscopy Study and Application in Photovoltaic Cell. *J. Phys. Chem. C* **2017**, *121*, 7015–7024.

(49) Rada, Z. H.; Abid, H. R.; Sun, H.; Shang, J.; Li, J.; He, Y.; Liu, S.; Wang, S. Effects of -NO₂ and -NH₂ functional groups in mixed-linker Zr-based MOFs on gas adsorption of CO₂ and CH₄. *Prog. Nat. Sci.: Mater. Int.* **2018**, *28*, 160–167.

(50) Dai, S.; Montero-Lanzuela, E.; Tissot, A.; Baldoví, H. G.; García, H.; Navalón, S.; Serre, C. Room temperature design of Ce(IV)-MOFs: from photocatalytic HER and OER to overall water splitting under simulated sunlight irradiation. *Chem. Sci.* **2023**, *14*, 3451–3461.

(51) Rueda-Navarro, C. M.; Ferrer, B.; Baldoví, H. G.; Navalón, S. Photocatalytic hydrogen production from glycerol aqueous solutions as sustainable feedstocks using Zr-based UiO-66 materials under simulated sunlight irradiation. *Nanomaterials* **2022**, *12*, 3808.

(52) Cabrero-Antonino, M.; Melillo, A.; Montero-Lanzuela, E.; Álvaro, M.; Ferrer, B.; Vayá, I.; Baldoví, H. G.; Navalón, S. Solar-driven gas phase photocatalytic CO₂ methanation by multimetallic UiO-66 solids decorated with RuO_x nanoparticles. *Chem. Eng. J.* **2023**, *468*, No. 143553.

(53) Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. Metal doping in cerium metal-organic frameworks for visible-response water splitting photocatalysts. *J. Chem. Phys.* **2019**, *150*, No. 041701.

(54) Rueda-Navarro, C. M.; Cabrero-Antonino, M.; Escamilla, P.; Díez-Cabanes, V.; Fan, D.; Atienzar, P.; Ferrer, B.; Vayá, I.; Maurin, G.; Baldoví, H. G.; et al. Solar-assisted photocatalytic water splitting using defective UiO-66 solids from modulated synthesis. *Nano Res.* **2024**, *17*, 4134–4150.

(55) Shearer, G. C.; Chavan, S.; Bordiga, S.; Svelle, S.; Olsbye, U.; Lillerud, K. P. Defect engineering: tuning the porosity and composition of the metal–organic framework UiO-66 via modulated synthesis. *Chem. Mater.* **2016**, *28*, 3749–3761.

(56) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.

(57) Santiago-Portillo, A.; Navalón, S.; Alvaro, M.; García, H. Generating and optimizing the catalytic activity in UiO-66 for aerobic oxidation of alkenes by post-synthetic exchange Ti atoms combined with ligand substitution. *J. Catal.* **2018**, *365*, 450–463.

(58) Sun, D.; Liu, W.; Qiu, M.; Zhang, Y.; Li, Z. Introduction of a mediator for enhancing photocatalytic performance via post-synthetic metal exchange in metal–organic frameworks (MOFs). *Chem. Commun.* **2015**, *51*, 2056–2059.

(59) Santaclara, J. G.; Olivos-Suarez, A. I.; Gonzalez-Nelson, A.; Osadchii, D.; Nasalevich, M. A.; van der Veen, M. A.; Kapteijn, F.; Sheveleva, A. M.; Veber, S. L.; Fedin, M. V.; et al. Revisiting the Incorporation of Ti(IV) in UiO-type metal–organic frameworks: Metal exchange versus grafting and their implications on photocatalysis. *Chem. Mater.* **2017**, *29*, 8963–8967.

(60) Wang, Y.; Li, H.; Zhou, W.; Zhang, X.; Zhang, B.; Yu, Y. Structurally disordered RuO₂ nanosheets with rich oxygen vacancies for enhanced nitrate electroreduction to ammonia. *Angew. Chem., Int. Ed.* **2022**, *61*, e202202604.

(61) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilsted, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. Synthesis and stability of tagged UiO-66 Zr-MOFs. *Chem. Mater.* **2010**, *22*, 6632–6640.

(62) Zhu, J.; Wu, L.; Bu, Z.; Jie, S.; Li, B.-G. Polyethyleneimine-modified UiO-66-NH₂(Zr) metal–organic frameworks: preparation and enhanced CO₂ selective adsorption. *ACS Omega* **2019**, *4*, 3188–3197.

(63) Nasalevich, M. A.; Van Der Veen, M.; Kapteijn, F.; Gascon, J. Metal-organic frameworks as heterogeneous photocatalysts: Advantages and challenges. *CrystEngComm* **2014**, *16*, 4919–4926.

(64) Hendrickx, K.; Vanpoucke, D. E. P.; Leus, K.; Lejaeghere, K.; Van Yperen-De Deyne, A. V.; Van Speybroeck, V.; Van Der Voort, P.; Hemelsoet, K. Understanding intrinsic light absorption properties of UiO-66 frameworks: A combined theoretical and experimental study. *Inorg. Chem.* **2015**, *54*, 10701–10710.

(65) Wu, X.-P.; Gagliardi, L.; Truhlar, D. G. Cerium metal–organic framework for photocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 7904–7912.

(66) Zhang, J.; Chen, H.; Duan, X.; Sun, H.; Wang, S. Photothermal catalysis: from fundamentals to practical applications. *Mater. Today* **2023**, *68*, 234–253.

(67) Zhang, X.; Li, X.; Zhang, D.; Su, N. Q.; Yang, W.; Everitt, H. O.; Liu, J. Product selectivity in plasmonic photocatalysis for carbon dioxide hydrogenation. *Nat. Commun.* **2018**, *8*, 14542.

(68) Luo, S.; Lin, H.; Wang, Q.; Ren, X.; Hernández-Pinilla, D.; Nagao, R.; Xie, Y.; Yang, G.; Li, S.; Song, H.; et al. Triggering water and methanol activation for solar-driven H₂ production: Interplay of dual active sites over plasmonic ZnCu alloy. *J. Am. Chem. Soc.* **2021**, *143*, 12145–12153.

(69) Ren, J.; Ouyang, S.; Xu, H.; Meng, X.; Wang, T.; Wang, D.; Ye, J. Targeting activation of CO₂ and H₂ over Ru-loaded ultrathin layered double hydroxides to achieve efficient photothermal CO₂ methanation in flow-type system. *Adv. Energy Mater.* **2016**, *7*, 1601657.

(70) Guo, C.; Tang, Y.; Yang, Z.; Zhao, T.; Liu, J.; Zhao, Y.; Wang, F. Reinforcing the efficiency of photothermal catalytic CO₂ methanation through integration of Ru nanoparticles with photothermal MnCo₂O₄ nanosheets. *ACS Nano* **2023**, *17*, 23761–23771.

(71) Xiong, K.; Wang, Y.; Zhang, F.; Li, X.; Lang, X. Linker length-dependent photocatalytic activity of β -ketoenamine covalent organic frameworks. *Appl. Catal. B-Environ* **2023**, *322*, No. 122135.

- (72) Yan, X.; Cao, M.; Li, S.; Duchesne, P. N.; Sun, W.; Mao, C.; Song, R.; Lu, Z.; Chen, X.; Qian, W.; et al. Visualizing the birth and monitoring the life of a bimetallic methanation catalyst. *J. Am. Chem. Soc.* **2023**, *145*, 27358–27366.
- (73) Beuls, A.; Swalus, C.; Jacquemin, M.; Heyen, G.; Karelavic, A.; Ruiz, P. CO₂ hydrogenation at low temperature over Rh/ γ -Al₂O₃ catalysts: Effect of the metal particle size on catalytic performances and reaction mechanism. *Appl. Catal., B* **2012**, *113–114*, 237–249.
- (74) Mateo, D.; Santiago-Portillo, A.; Albero, J.; Navalón, S.; Alvaro, M.; García, H. Long-term photostability in terephthalate metal-organic-frameworks. *Angew. Chem., Int. Ed.* **2019**, *58*, 17843–17848.
- (75) Mateo, D.; Cerrillo, J. L.; Durini, S.; Gascon, J. Fundamentals and applications of photo-thermal catalysis. *Chem. Soc. Rev.* **2021**, *50*, 2173–2210.
- (76) Khan, I. S.; Garzon-Tovar, L.; Mateo, D.; Gascon, J. Metal-organic-frameworks and their derived materials in photo-thermal catalysis. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202200316.
- (77) Song, C.; Wang, Z.; Yin, Z.; Xiao, D.; Ma, D. Principles and applications of photothermal catalysis. *Chem. Catalysis* **2022**, *2*, 52–83.
- (78) Ruckebusch, C.; Sliwa, M.; Pernot, P.; de Juan, A.; Tauler, R. Comprehensive data analysis of femtosecond transient absorption spectra: A review. *J. Photochem. Photobiol. C* **2012**, *13*, 1–27.
- (79) Ma, X.; Wang, L.; Zhang, Q.; Jiang, H.-L. Switching on the photocatalysis of metal–organic frameworks by engineering structural defects. *Angew. Chem., Int. Ed.* **2019**, *58*, 12175–12179.
- (80) Xiao, J.-D.; Shang, Q.; Xiong, Y.; Zhang, Q.; Luo, Y.; Yu, S.-H.; Jiang, H.-L. Boosting photocatalytic hydrogen production of a metal–organic framework decorated with platinum nanoparticles: The platinum location matters. *Angew. Chem., Int. Ed.* **2016**, *128*, 9535–9539.
- (81) Cabrero-Antonino, M.; Melillo, A.; Montero-Lanzuela, E.; Álvaro, M.; Ferrer, B.; Vayá, I.; Baldoví, H. G.; Navalón, S. Solar-driven gas phase photocatalytic CO₂ methanation by multimetallic UiO-66 solids decorated with RuOx nanoparticles. *Chem. Eng. J.* **2023**, *468*, No. 143553.
- (82) Melillo, A.; Cabrero-Antonino, M.; Navalón, S.; Álvaro, M.; Ferrer, B.; García, H. Enhancing visible-light photocatalytic activity for overall water splitting in UiO-66 by controlling metal node composition. *Appl. Catal., B* **2020**, *278*, No. 119345.
- (83) Bhattacharyy, A.; Gutiérrez, M.; Cohen, B.; Szalad, H.; Albero, J.; García, H.; Douhal, A. Unraveling the optimal cerium content for boosting the photoresponse activity of mixed-metal Zr/Ce-based metal–organic frameworks through a photodynamic and photocurrent correlation: Implications on water splitting efficiency. *ACS Appl. Mater. Interfaces* **2023**, *15*, 36434–36446.
- (84) Bhattacharyya, A.; Gutiérrez, M.; Cohen, B.; Valverde-González, A.; Iglesias, M.; Douhal, A. How does the metal doping in mixed metal MOFs influence their photodynamics? A direct evidence for improved photocatalysts. *Mater. Today Energy* **2022**, *29*, No. 101125.
- (85) Yu, X. M.; Li, J.; Du, M. H.; Song, X. J.; Huang, H. L.; Nie, L. Adaptive lattice-matched MOF and COF core–shell heterostructure for carbon dioxide photoreduction. *Cell Rep. Phys. Sci.* **2023**, *4*, No. 101657.
- (86) L, M.; Schirato, A.; Montini, T.; Alabastri, A.; Naldoni, A.; Fornasiero, P. Challenges in temperature measurements in gas-phase photothermal catalysis. *Joule* **2022**, *6*, 1727–1742.
- (87) Liu, L.; Zhong, K.; Meng, L.; Hemelrijck, D. V.; Wang, L.; Glorieux, C. Temperature-sensitive photoluminescent CdSe-ZnS polymer composite film for lock-in photothermal characterization. *J. Appl. Phys.* **2016**, *119*, 224902.
- (88) Douma, F.; Lakiss, L.; Lebedev, O. I.; Cardin, J.; Kostov, K. L.; El Fallah, J.; Valtchev, V.; El-Roz, M. Silver quasi-nanoparticles: bridging the gap between molecule-like clusters and plasmonic nanoparticles. *Mater. Adv.* **2021**, *2* (16), 5453–5464.
- (89) Hadjiivanov, K.; Lavalley, J.-C.; Lamotte, J.; Maugé, F.; Saint-Just, J.; Che, M. FTIR Study of CO Interaction with Ru/TiO₂ catalysts. *J. Catal.* **1998**, *176* (2), 415–425.
- (90) Su, B.; Kong, Y.; Wang, S.; Zuo, S.; Lin, W.; Fang, Y.; Hou, Y.; Zhang, G.; Zhang, H.; Wang, X. Hydroxyl-bonded Ru on metallic TiN surface catalyzing CO₂ reduction with H₂O by infrared light. *J. Am. Chem. Soc.* **2023**, *145*, 27415–27423.
- (91) Wang, Y.; Liu, Y.; Tan, L.; Lin, X.; Fang, Y.; Lu, X. F.; Hou, Y.; Zhang, G.; Wang, S. Confining ultrafine Pt nanoparticles on In₂O₃ nanotubes for enhanced selective methanol production by CO₂ hydrogenation. *J. Mater. Chem. A* **2023**, *11*, 26804–26811.
- (92) Kattel, S.; Liu, P.; Chen, J. G. Tuning selectivity of CO₂ hydrogenation reactions at the metal/oxide interface. *J. Am. Chem. Soc.* **2017**, *139*, 9739–9754.
- (93) El-Roz, M.; Lakiss, L.; Telegeiev, I.; Lebedev, O.; Bazin, P.; Vicente, A.; Fernandez, C.; Valtchev, V. High-visible-light photo-activity of plasma-promoted vanadium clusters on nanozeolites for partial photooxidation of methanol. *ACS Appl. Mater. Interfaces* **2017**, *9* (21), 17846–17855.
- (94) Hamoud, H.; Wolski, L.; Abdelli, H.; Chtourou, R.; Lebedev, O.; Martin, C.; Fan, D.; Maurin, G.; Maignan, A.; El-Roz, M. Earth-abundant-based photocatalysts for efficient and selective H₂ production through reforming of formic acid under visible light. *ACS Catal.* **2023**, *13* (24), 16266–16278.
- (95) Guglielminotti, E.; Boccuzzi, F.; Manzoli, M.; Pinna, F.; Scarpa, M. Ru/ZrO₂ Catalysts: I. O₂, CO, and NO adsorption and reactivity. *J. Catal.* **2000**, *192* (1), 149–157.
- (96) Hamoud, H. I.; Wolski, L.; Abdelli, H.; Chtourou, R.; Lebedev, O.; Martin, C.; Fan, D.; Maurin, G.; Maignan, A.; El-Roz, M. Earth-abundant-based photocatalysts for efficient and elective H₂ production through reforming of formic acid under visible light. *ACS Catal.* **2023**, *13* (24), 16266–16278.
- (97) El-Roz, M.; Lakiss, L.; Telegeiev, I.; Lebedev, O. I.; Bazin, P.; Vicente, A.; Fernandez, C.; Valtchev, V. High-visible-light photo-activity of plasma-promoted vanadium clusters on nanozeolites for partial photooxidation of methanol. *ACS Appl. Mater. Interfaces* **2017**, *9* (21), 17846–17855.
- (98) Aldana, P. U.; Ocampo, F.; Kobl, K.; Louis, B.; Thibault-Starzyk, F.; Daturi, M.; Bazin, P.; Thomas, S.; Roger, A. Catalytic CO₂ valorization into CH₄ on Ni-based ceria-zirconia. Reaction mechanism by operando IR spectroscopy. *Catal. Today* **2013**, *215*, 201–207.
- (99) Morgan, G. A., Jr; Sorescu, D. C.; Zubkov, T.; Yates, J. T., Jr The Formation and stability of adsorbed formyl as a possible intermediate in Fischer–Tropsch chemistry on ruthenium. *J. Phys. Chem. B* **2004**, *108* (11), 3614–3624.
- (100) Finocchio, E.; Daturi, M.; Binet, C.; Lavalley, J.; Blanchard, G. Thermal evolution of the adsorbed methoxy species on Ce_xZr_{1-x}O₂ solid solution samples: a FT-IR study. *Catal. Today* **1999**, *52* (1), 53–63.
- (101) Schild, C.; Wokaun, A.; Baiker, A. On the mechanism of CO and CO₂ hydrogenation reactions on zirconia-supported catalysts: a diffuse reflectance FTIR study: Part I. Identification of surface species and methanation reactions on palladium/zirconia catalysts. *J. Mol. Catal.* **1990**, *63* (2), 223–242.
- (102) Issa Hamoud, H.; Wolski, L.; Pankin, I.; Bañares, M. A.; Daturi, M.; El-Roz, M. In situ and operando spectroscopies in photocatalysis: Powerful techniques for a better understanding of the performance and the reaction mechanism. *Top. Curr. Chem.* **2022**, *380* (5), 37.