

Special Issue

Pivotal Role of Holes in Photocatalytic CO₂ Reduction on TiO₂

 Nikolaos G. Moustakas,^[a] Felix Lorenz,^[a] Martin Dilla,^[b] Tim Peppel,^[a] and Jennifer Strunk*^[a]

Abstract: Evidence is provided that in a gas-solid photocatalytic reaction the removal of photogenerated holes from a titania (TiO₂) photocatalyst is always detrimental for photocatalytic CO₂ reduction. The coupling of the reaction to a sacrificial oxidation reaction hinders or entirely prohibits the formation of CH₄ as a reduction product. This agrees with earlier work in which the detrimental effect of oxygen-evolving cocatalysts was demonstrated. Photocatalytic alcohol oxidation or even overall water splitting proceeds in these

reaction systems, but carbon-containing products from CO₂ reduction are no longer observed. H₂ addition is also detrimental, either because it scavenges holes or because it is not an efficient proton donor on TiO₂. The results are discussed in light of previously suggested reaction mechanisms for photocatalytic CO₂ reduction. The formation of CH₄ from CO₂ is likely not a linear sequence of reduction steps but includes oxidative elementary steps. Furthermore, new hypotheses on the origin of the required protons are suggested.

Introduction

More than forty years have passed since the discovery of photocatalytic and photoelectrochemical reduction of CO₂ on TiO₂ and other semiconductors.^[1] Just like overall water splitting, this reaction promises the formation of a storable fuel with only (sun)light as energy input. In both reactions, water splitting and CO₂ reduction, the desired product is a result of the reduction reaction only, but the stoichiometry necessarily requires forming an oxidation product, too. The straightforward oxidation product is gaseous O₂ resulting from the oxidation of H₂O. It is well known that it is the more challenging of the two half reactions, particularly on TiO₂.^[2] For scientific purposes, it is possible to replace the challenging H₂O oxidation reaction with the oxidation of a sacrificial donor, but since the overall reaction then usually becomes thermodynamically favorable ($\Delta G < 0$), energy storage is no longer achieved, and in addition the reaction has no more economic potential. The fate of the photogenerated holes as oxidizing equivalents must thus be understood and controlled, so that either O₂ can be evolved, or

another industrially relevant oxidation reaction can be performed and coupled to CO₂ reduction.

A previous work by some of us^[3] has shown that in a gas-solid photocatalytic process TiO₂ is able to react with some yet unknown type of oxygen species liberated in the course of CO₂ reduction, thereby stoichiometrically consuming the oxidation equivalents. Consequently, both reduction and oxidation reactions can only proceed until the TiO₂ is saturated with those oxygen species. In an uninterrupted reduction reaction of CO₂ in dilute concentration in a continuous flow, this saturation process takes more than 12 h due to the small yields of the reduction reaction.^[3] This may explain why many scientific articles – including some of our own works^[4] – have previously been published that do not present any oxidation product.^[5] Our attempts to facilitate O₂ evolution with Ir or Co oxide cocatalysts on TiO₂ was only partially successful: An active photocatalyst for overall splitting of gaseous H₂O was obtained, but not a trace of any carbon-containing reduction product was observed with this system.^[3] This can either be rationalized by a rapid reoxidation of the formed hydrocarbons by the O₂ now liberated into the gas phase, or by a reaction mechanism previously suggested by Shkrob et al. This so-called “glyoxal mechanism” does not involve a “linear” series of successive reduction steps, but also includes oxidation reactions such as the oxidation of acetaldehyde to an acetyl radical and then to a methyl radical through decarbonylation.^[2a,6] If this mechanism is in operation under our reaction conditions – and previous results indicate that this is the case^[4b] – then CH₄ formation is no longer possible when the holes are consumed for another reaction. Based on our previous results with the oxygen evolving cocatalysts, it was not possible to distinguish between the two explanations of rapid hydrocarbon oxidation on the one hand, or a pivotal role of holes in the reaction mechanism from CO₂ to CH₄ on the other hand because it requires removing the photogenerated holes without at the same time producing O₂.

[a] Dr. N. G. Moustakas, F. Lorenz, Dr. T. Peppel, Prof. Dr. J. Strunk
 Department of Heterogeneous Photocatalysis
 Leibniz-Institute for Catalysis (LIKAT)
 Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
 E-mail: jennifer.strunk@catalysis.de

[b] Dr. M. Dilla
 Max Planck Institute for Chemical Energy Conversion
 Stiftstr. 34–36, 45470 Mülheim an der Ruhr (Germany)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202103070>

Part of a Special Issue on Contemporary Challenges in Catalysis.

© 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Here, results of such an attempt to reduce CO_2 but circumvent O_2 evolution are presented. Two different approaches are followed: Firstly, the coupling of CO_2 reduction to the oxidation of an alcohol is attempted. Alternatively, H_2 is added to the reaction mixture, to remove the holes and the formed oxygen species by the formation of H_2O . It will be shown that any hole scavenger reduces or even entirely inhibits the formation of carbon-based reaction products. It is concluded that the holes have a pivotal role in the reaction of CO_2 to CH_4 , so that a full separation of oxidation and reduction reaction on bare TiO_2 is likely impossible.

Results and Discussion

All measurements were performed with commercial TiO_2 P25 (Evonik Industries, anatase:rutile = ~80:20) in our high-purity gas-phase photoreactor presented elsewhere^[4,7] and briefly described in the Supporting Information (Figure S1 in Supporting Information). Photocatalytic CO_2 reduction on P25 has been performed extensively in our previous works. It has been found reproducibly that under our standard conditions (1.5% CO_2 and 6,000 ppm H_2O in He, batch reaction) CH_4 is the main reaction product, and the concentration in the reactor amounts to ~80 ppm after six hours. Aside from CH_4 , roughly 20 ppm CO and ~15 ppm of H_2 are formed.^[4b]

Before presenting the results of the current study, we would like to briefly summarize the results of a previous study conducted under reaction conditions of continuous flow.^[3] On bare P25 (70 mg in powder form), CH_4 was formed for a total of ~14 h, with the production rate steadily declining after ~8 h. No O_2 formation was observed, but the stoichiometry of the reaction would have required the formation of 78 nmol of O_2 in those ~14 hours. When P25 was modified with Ir oxide ($\text{IrO}_x/\text{TiO}_2$), the resultant material did not reduce CO_2 at all, but performed overall H_2O splitting in presence of CO_2 . In a pure H_2O splitting experiment, stoichiometric production of H_2 and O_2 in the expected 2:1 ratio was observed, but in the early stages of the experiment, the formation of O_2 was substoichiometric. Certain amounts of O_2 appeared to be missing in the gas phase compared to the expected stoichiometric ratio. Integration of the curve yielded an amount of ~103 nmol of vanished O_2 . Considering the differing calcination temperatures of the two materials (P25 and $\text{IrO}_x/\text{TiO}_2$) and the relatively large error of this estimation, a relatively good fit of these two values can be assumed. It was concluded that the used 70 mg of TiO_2 can store O_2 in an order of magnitude of 100 nmol, and CO_2 reduction runs only until TiO_2 is saturated. In the previous publication, it was not possible to give a conclusive explanation on the fate of the holes, or why the $\text{IrO}_x/\text{TiO}_2$ sample was unable to reduce CO_2 to CH_4 or any other carbon-containing product.

In the current study, oxidation reactions other than the challenging oxidation reaction of H_2O were attempted, which at the same time prevented the formation of the byproduct O_2 . Figure 1a displays the results of a co-reaction of CO_2 with small amounts of ethanol (EtOH) on P25 under batch conditions.

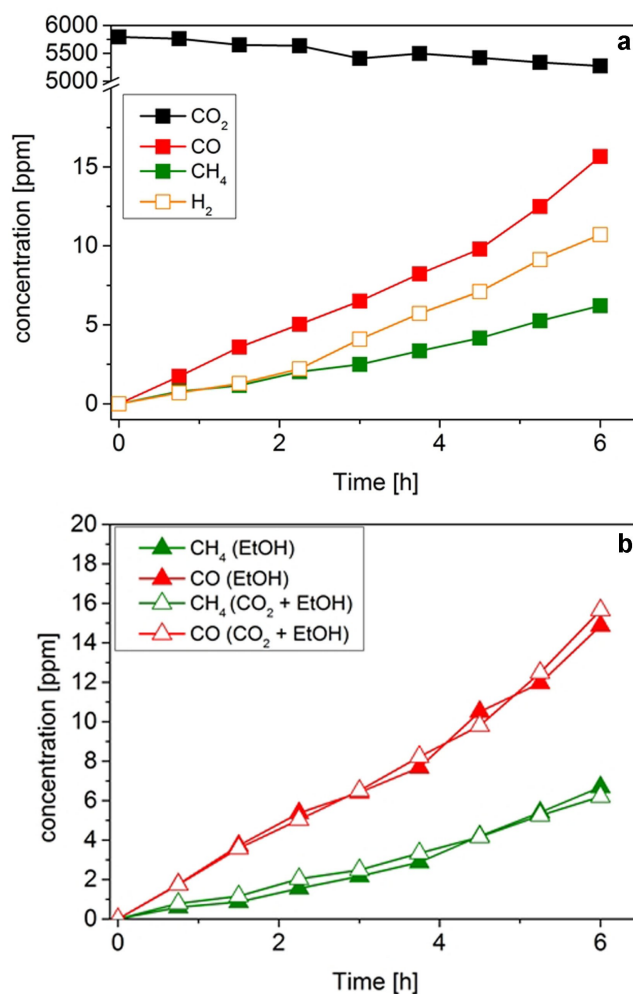


Figure 1. (a) Photocatalytic CO_2 reduction (1.5% CO_2 in He) in batch mode over P25 impregnated with aqueous EtOH solution; (b) comparison of the amounts of CO and CH_4 formed in reaction of EtOH on P25 with and without 1.5% CO_2 present in the gas phase.

Please note that small amounts of H_2O are also present in this reaction. The gas chromatograms of the product mixtures reveal a concentration of ~15 ppm CO, ~10 ppm H_2 and ~5 ppm CH_4 after 6 h of reaction time. When the same reaction is performed in absence of CO_2 and the amounts of the carbon-containing products are compared (Figure 1b), they turned out to be identical. Therefore, it becomes obvious that none of these products is formed from CO_2 , but the entire amount of the formed CO and CH_4 solely results from a decomposition reaction of EtOH. Thus, the presence of EtOH entirely suppresses the reduction reaction of CO_2 . It also becomes obvious that EtOH is likely not selectively oxidized under the given reaction conditions but is entirely fragmented into C_1 compounds. The gas chromatograph (GC) used for these experiments (Shimadzu TRACERA equipped with barrier discharge ionization detector, BID) was calibrated for CO, CH_4 , CO_2 , H_2 and H_2O , and would additionally have detected C_2 and C_3 hydrocarbons, which were, however, not observed.

Additional experiments have been performed using isopropanol (i PrOH) instead of EtOH, and another GC was used (*Shimadzu TRACERA* with BID and additional flame ionization detector, FID) which can detect hydrocarbon products up to a chain length of C_{14} . For these experiments, 100 μ l of i PrOH were added dropwise onto the surface of the P25 pellet sample in the photoreactor using a microliter pipette. Figure 2 shows the main products of the photocatalytic reaction in the presence and absence of CO_2 . Although a variety of other products such as ethylene (C_2H_4) and some yet unidentified compounds were formed (Figure S2 in Supporting Information), the main products comprise ethane (C_2H_6), CH_4 and CO. Here, the presence of CO_2 even reduces the amount of formed carbon-containing products, hinting to a direct competition of CO_2 and alcohol molecules for the photogenerated holes.

Furthermore, the intense blue color of the TiO_2 pellet after the reaction (Figure S3 in Supporting Information) indicates that significantly more holes have been consumed than electrons because the blue color is commonly explained with a reduction of the material, or in other words, an accumulation of excess electrons, which leads to the formation of Ti^{3+} .^[8] The blue color of the pellet was interestingly observed also on its non-directly irradiated surface as well as in the cross-section of the pellet. As the P25 pellet was not directly in contact with the reaction chamber bottom but was placed on top of a quartz plate, the reflected light can explain the blue color of the bottom side of the pellet. An oxygen vacancy migration effect can be assumed for the blue color of the cross-section, as the i PrOH deposited on the surface (top side) of the pellet was also soaked into the bulk of the P25 pellet. After the end of the i PrOH oxidation experiment the pellet was removed from the photoreactor and its optical properties were examined (Figure S4 in Supporting Information). No change in the optical band-gap (E_g) could be identified. In contact with the atmospheric air, the pellet became pale blue, but it did not

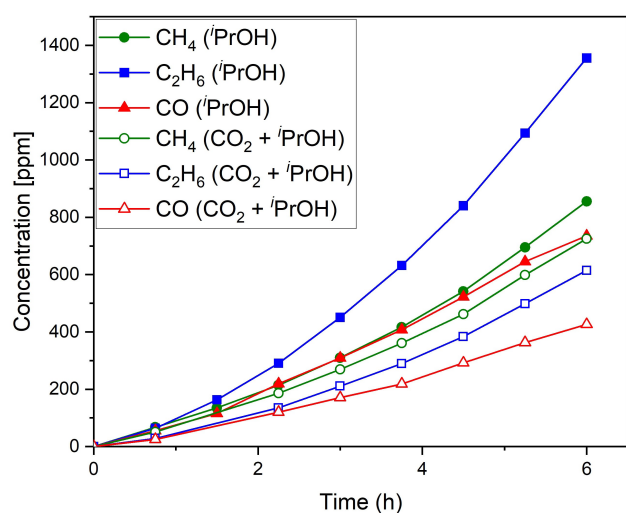


Figure 2. Comparison of the amounts of C_2H_6 , CH_4 and CO formed in reaction of i PrOH on P25 with and without 1.5% CO_2 present in the gas phase.

completely return to its original white color as it can be seen from the flattening of the wide absorption band in the visible range. Reoxidation to full white color of the pellet was only achieved by heating it up in air to 150 °C.

Two additional P25 pellets were pressed, and the effect of TiO_2 pre-reduction was further studied. Each of the two pellets was used for the oxidation of i PrOH, leading to a blue-colored pellet. Additionally, degradation products of i PrOH have likely been accumulated on the surface. Subsequently, one of the two blue pellets was used as a photocatalyst for a CO_2 reduction experiment (addition of CO_2 and H_2O), whereas the other was used as a reference photocatalyst to which only He and H_2O were offered. These experiments in presence or absence of CO_2 provide an indirect proof of the origin of the identified products.

The formed products with and without CO_2 are presented in Figure 3. The concentrations of CH_4 and C_2H_6 appear to be similar regardless of the presence of CO_2 . This confirms the origin of these products from the further degradation of i PrOH-derived intermediates on the surface, as opposed to their origin from CO_2 . For CO, a small decrease can be observed when CO_2 is introduced in the reactor. This may indicate a small influence of CO_2 on the specific mechanisms of the surface processes involving the i PrOH degradation products. As in the case of EtOH, it is evident that all identified products originate from the decomposition of i PrOH and not from CO_2 . So, in spite of reduced (oxygen vacancy-rich) TiO_2 having been suggested as superior photocatalyst,^[9] CO_2 reduction does not proceed if the photocatalyst is simultaneously degrading organic surface species, i.e. performs an oxidation reaction.

Next, the effect of H_2O and H_2 in the gas phase on the CH_4 formation was evaluated. Please note that the results presented in the following have been obtained in a series of consecutive

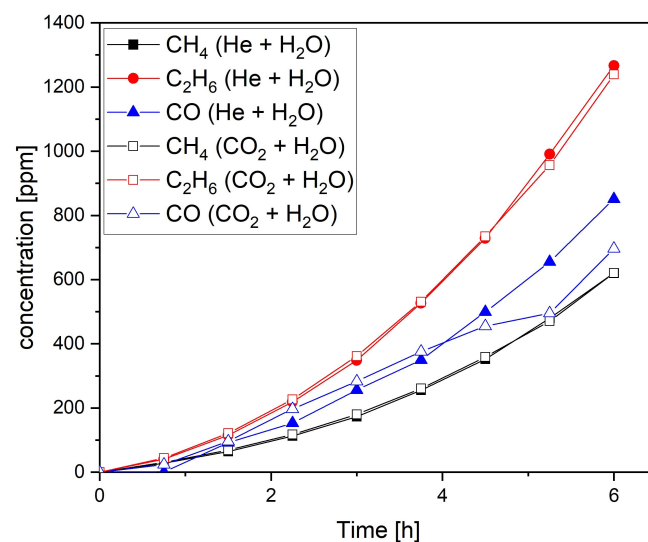


Figure 3. Amounts of major products formed in a photocatalytic CO_2 reduction experiment (1.5% CO_2 in He, 6,000 ppm H_2O , Hg/Xe lamp, light intensity 200 $mW cm^{-2}$) using P25 pellets that had previously been used for i PrOH oxidation. A similar reaction without the presence of CO_2 is used as comparison.

experiments using the same P25 sample (50 mg in powder form) without any cleaning steps in-between to remove the adsorbates on the surface of the material, such as reaction intermediates and/or products. Figure 4 shows the effect of a variation of the H₂O content under batch reaction conditions. Reacting CO₂ on P25 without adding H₂O resulted in a CH₄ concentration of 120 ppm after 6 h (Figure 4, blue line and triangles), which was already more than under the standard reaction conditions with 6,000 ppm H₂O in the gas phase.^[4b] This corresponds well to similar experiments conducted previously under flow conditions.^[10] It is well known in the literature that under ambient conditions, the oxide surfaces can be covered by up to 20 layers of H₂O.^[11] This allows TiO₂ to perform the photoreduction of CO₂ without the need for the addition of extra amounts of H₂O in the gas phase. In a consecutive run without adding H₂O, CH₄ formation was even more enhanced, in which the 120 ppm were already formed in less than 4 h (Figure 4, grey circles and line). This may be attributable to the three following explanations: (i) The first measurement may have dried the TiO₂ even further because some of the water was consumed in the reaction, and/or (ii) in a second reaction, a carbon pool was already present on the TiO₂ surface, which could also contribute to product formation in a second run, and/or (iii) if less H₂O is present, less holes are consumed, which are then available for the CO₂ reduction pathway.

A drier surface according to explanation (i) can result in more CO₂ molecules being adsorbed on TiO₂ which in turn can lead to higher product yields. On TiO₂, the adsorption of H₂O is more favorable than the adsorption of CO₂,^[12] so in presence of larger amounts of H₂O, it may block CO₂ from adsorbing in sufficient amounts. The explanation (ii) of the formation of a "carbon pool", previously suggested for TiO₂/SiO₂^[4a] and TiO₂,^[4b] is supported by the consecutive measurement in Figure 4, in which H₂O was added again to the gas phase, and product

formation was even more enhanced (Figure 4, black squares and line). Although water is now present in the gas phase again, the formed carbon pool makes the reaction conditions relatively carbon-rich, particularly near the surface. The carbon pool can consist either of products not able to desorb from the material under the selected experimental conditions, or of intermediate states along the reaction pathway. When H₂O is added, the latter might eventually be converted to CH₄. In this respect, in another consecutive experiment, CH₄ formation was even higher, allowing to reach a concentration of more than 320 ppm in the reactor. This can be converted to a yield of 0.1% g_{cat}⁻¹ h⁻¹, which is the highest yield so far obtained with TiO₂ in our gas-solid photoreactor when only CO₂ and H₂O were used as reactants. With the estimated reactor volume of 25 ml, this yield, obtained with 50 mg TiO₂, can be converted to ~1.1 μmol g_{cat}⁻¹ h⁻¹.

It is also remarkable about the obtained results in Figure 4 that after a short induction period, the increase in CH₄ concentration in all four experiments is linear and does not start to level off as previously observed.^[4b] This indicates that the CO₂ reduction reaction can run unperturbed for longer periods of time under relatively carbon-rich as opposed to water-rich conditions. In this respect, it should also be noted that the total amount of CH₄ formed in all four experiments together amounts to ~0.80 μmol, which is much more than the 39 nmol previously observed under conditions of continuous flow in a comparable time frame and with an almost comparable sample amount (70 mg).^[10] While a detailed discussion of the implications of these observations with respect to reaction engineering is beyond the scope of this study, these results may indicate that a higher residence time is beneficial for the very slow reaction, or that the helium purging conducted in between the experiments removes some inhibiting species, such as oxygen-related byproducts.

Altogether, the following conclusions can be drawn: If only low amounts of adsorbed water are present, relatively more CO₂ will be adsorbed on the surface, thereby enhancing product formation. However, once the surface becomes too dry, not sufficient protons are still available to finish the reaction sequence to CH₄, so the surface will be covered by partially hydrogenated intermediates ("carbon pool"). Then, water dosing is beneficial, indicating that water is indeed involved in the overall reaction from CO₂ to CH₄ as proton source, but without evolving oxygen, as we have previously suggested from experiments under continuous flow.^[10] It can also be ruled out that the primary role of water is hole scavenging because then the dosage of alcohols and water should influence product formation from photocatalytic CO₂ reduction in a similar manner, which it clearly did not do: The addition of alcohols completely inhibited CO₂ reduction.

This leads to the question whether another potential source of protons, or, more generally speaking, hydrogen atoms, can improve product formation when partially hydrogenated intermediates are already present on the surface. So, after the reaction sequence displayed in Figure 4, the addition of H₂ was studied. Here, too, consecutive reaction cycles were run so that the sample became more and more depleted of H₂O (Figure 5).

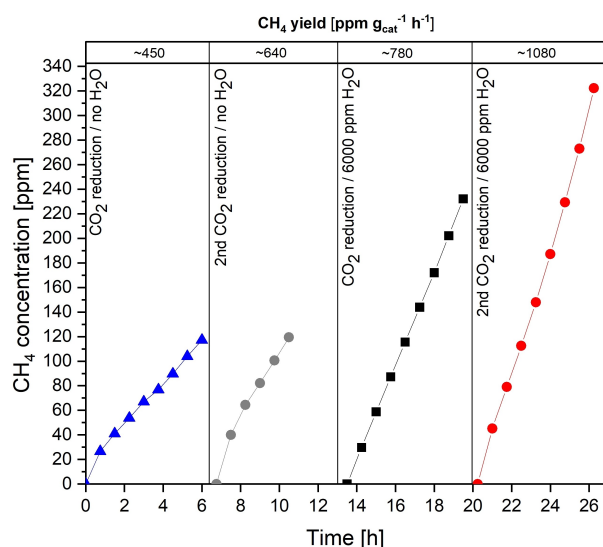


Figure 4. Consecutive CO₂ reduction experiments with variation of the H₂O content in the gas phase.

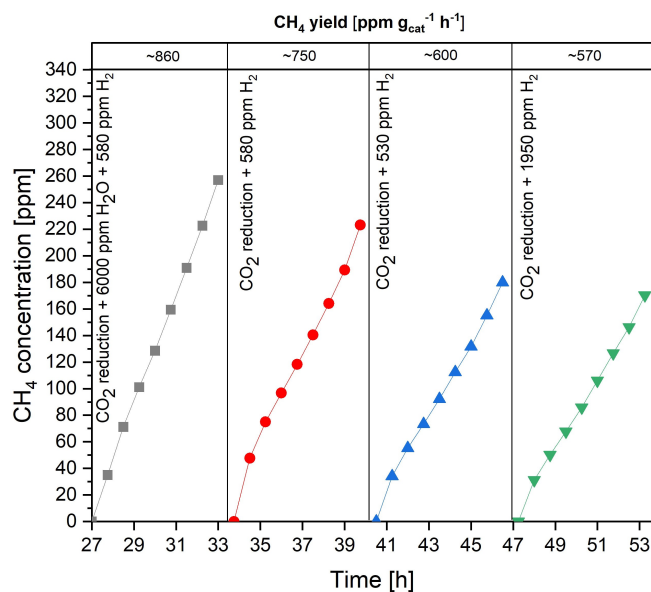


Figure 5. Effect of the addition of H₂ on photocatalytic CO₂ reduction under batch reaction conditions.

The first measurement in Figure 5 (gray squares and line), conducted after the fourth measurement in Figure 4 (red circles and line), featured almost the same reaction conditions, with the sole difference that 580 ppm of H₂ were additionally present in the gas phase. Surprisingly, the yield of CH₄ was lower than in the corresponding measurement without H₂. Removing the H₂O from the gas phase (second measurement in Figure 5, red circles and line) had a slightly detrimental effect, although it was beneficial in the absence of H₂. Slightly decreasing (Figure 5, blue triangles and line) or increasing (Figure 5, green triangles and line) the concentration of H₂ hardly affected CH₄ formation, but certainly did not promote it. In all measurements in Figure 5, a total of ~0.84 μmol of CH₄ were formed, again indicating that a cyclic operation, with purging steps in between batch experiments, may be the preferred mode of reactor operation. While in all measurements presented in Figures 4 and 5 CH₄ was the main product, traces of ethane (< 3 ppm) were also identified. The formation of ethane can hint that a C₂ mechanism takes place in the CO₂-to-CH₄ photoconversion.

The detrimental, or at best inert, role of H₂ in the reaction indicates that it is not an effective proton source. Potentially, TiO₂ does not feature sites for H₂ splitting, or H₂ is not an efficient hole trap on TiO₂. The latter would also explain why H₂ suppresses CO₂ reduction only partially, and not completely. To ensure that the tested photocatalysts remain stable during the respective experiments an XRD analysis was performed for the P25 used in ¹PrOH oxidation and the one used in the study of the effect of H₂O and H₂ in CO₂ photoreduction. As it can be seen in Figure S5 (Supporting Information), the X-ray diffractograms reveal that the photocatalysts were not structurally affected by the applied experimental conditions.

Together with our previous results on IrO_x/TiO₂ (see above), the obtained results evidence that the removal of holes from TiO₂ suppresses the CO₂ reduction reaction to CH₄ as a final product. Since O₂ is not formed in any of the reactions studied here, a rapid reoxidation of the formed hydrocarbons cannot explain the observations. Instead, a direct participation of holes in the reaction pathway is the more likely scenario.

At a first glance, these results seem implausible. CO₂ contains the C atom in the highest oxidation state, hence further oxidation is impossible. Based on extensive EPR experiments, Shkrob et al.^[6] have suggested that in the course of CO₂ reduction, various organic molecules are formed and reoxidized on the surface, whereby some stable C₂ intermediates, namely glyoxal, glycolaldehyde and acetaldehyde are also being formed. Only the latter are eventually converted to liberate CH₄, which cannot be obtained on any pathway involving only C₁ intermediates. The final reaction steps of this sequence involve the reaction of acetaldehyde with a photogenerated hole, to liberate CO and a methyl radical. The latter then abstracts a H atom from a suitable donor, to eventually generate CH₄. Alternatively, glycolaldehyde may react with a hole to CO and a hydroxymethylene radical, whereby the latter first disproportionates to methanol (MeOH) and formaldehyde. MeOH then reacts with formate to methylformate that can also liberate a methyl radical which eventually ends up in CH₄. Both pathways involve holes, so the more efficiently the holes are removed from TiO₂, the more efficiently the CH₄ formation will be prevented. The reaction sequence by Shkrob et al. has been evaluated for (frozen) acidic aqueous solution of TiO₂, but evidence for a similar mechanism in the gas-solid process has previously been obtained by us,^[4b] in particular with respect to the involved reaction of acetaldehyde. Another possibility may be an involvement of carbonates or bicarbonates, which have previously been found to compete with H₂O for the photogenerated holes.^[13] Although we observed in our previous study a negative influence of a stabilization of carbonates on the surface of TiO₂ by Na doping, we also clearly saw a change in the coordination of the carbonate and carboxylate species to the surface.^[4b] It is, thus, possible that formerly active intermediates in the reaction pathway have been transformed to excessively stable inactive spectator species by the surface doping with Na.

The consecutive reactions under carbon pool formation (Figures 4 and 5) require additional consideration. If gaseous H₂O is not fed to the reactor, the adsorbed water will be consumed, but not be replaced. So, the surface will become depleted of protons, which eventually also inhibits CH₄ formation. Hence, an addition of H₂O after carbon pool formation has taken place has a beneficial effect. H₂ addition cannot compensate for this loss of protons (Figure 5), but affects the reaction negatively, if it does so at all.

All in all, the results suggest that H₂O is still the best co-reactant ("reductant") for CO₂ from those studied here (H₂O, alcohol, H₂), although yields remain low. H₂O should also be a hole scavenger, but it is known that this reaction is unfavorable on TiO₂, most obviously evidenced by the inability of TiO₂ to evolve O₂. In the light of the observations made here, the slow and unfavorable reaction of water with photogenerated holes

may be the primary reason why it is the only effective co-reactant. This also indicates that H₂O is possibly not actively participating in the photoreaction but is instead deprotonated by a suitably reactive (i.e. Brønsted basic) surface intermediate. Alternatively, hydroxyl groups on the surface of TiO₂ might be the only efficient proton donors, and the dissociative adsorption of H₂O at oxygen vacancies may recreate some of them. This would also be in accordance with the overall function of TiO₂ as oxygen-scavenging reaction partner as suggested previously.^[3]

Further work, particularly involving in situ optical and vibrational spectroscopy, may clarify the open questions with regard to the sequence of surface intermediates and the location of the holes, but the economic sense of such studies must be put to question. It becomes more and more evident that overall photocatalytic CO₂ reduction cannot be realized with TiO₂, so research on alternative photocatalysts appears more promising in the future.

Conclusion

It has been shown that the addition of alcohols as hole scavengers to TiO₂ does not improve photocatalytic CO₂ reduction in a high-purity gas-solid reaction system. Instead, CO₂ reduction is entirely prevented. The blue color of the catalyst after alcohol oxidation confirms the net reduction of TiO₂, but even a subsequent CO₂ reduction reaction on this blue titania does not lead to the observation of CO₂ reduction products. Together with our earlier observations that enforcing O₂ evolution by Ir oxide cocatalysts inhibits CO₂ reduction, the results are a strong indication that holes have a pivotal role in the CO₂ reduction mechanism to CH₄, possibly by oxidizing intermediates such as acetaldehyde and glycolaldehyde. In addition, it has been confirmed that CH₄ yields are higher in the absence of gaseous H₂O, but after the formation of a carbon pool on the surface H₂O is required as a proton donor. H₂ is a less efficient proton donor, most probably because its splitting is not facile on TiO₂. The results also indicate that H₂O is potentially not an active participant in the reaction, for example, by scavenging holes, but is possibly deprotonated by a sufficiently reactive carbon-based surface intermediate.

Experimental Section

Two different generations of our home-made high-purity photo-reactor setups were used for the experiments as explained in Ref. [7]. A brief description is provided in the Supporting Information. In all studies, the samples (in powder or in pellet form) were irradiated by a 200 W Hg-Xe arc lamp (Newport) for a total duration of 6 h. A water-based IR filter was utilized in the light pathway to avoid excessively heating up of the sample. Reactions were run in batch mode with an initial pressure of 1.5 bar inside the reactor. Gaseous samples were collected every 45 min and were analyzed using gas chromatography.

To study the reaction of EtOH on bare TiO₂ (P25), the oxide in powder form (70 mg) was first impregnated with a few drops of a

highly dilute aqueous EtOH solution (0.5 ml EtOH in 500 ml H₂O), similar to the procedure with MeOH described in Ref. [4b]. After drying in air, the sample was introduced into the photoreactor. Subsequently, the photoreaction was either carried out in a pure He atmosphere, or in the presence of 1.5% CO₂.

For the study of the effect of ¹PrOH on TiO₂, 1 g of P25 was pressed at 2 bar for 15 min to form a dense pellet (3 cm in diameter). This pellet was inserted into the reaction chamber of the high-purity photoreactor and 100 μl of ¹PrOH (99.5%, extra dry over molecular sieve, Acros Organics) were added dropwise onto the pellet. The reaction chamber was then flushed with the appropriate gas mixture (pure He or 1.5% CO₂ in He) for 2 h until no O₂ could be detected. Afterwards the reactor was filled with the gas mixture up to a final pressure of 1.5 bar and was further operated under batch conditions. In the study of H₂ and/or H₂O dosing in CO₂ photo-reduction, 50 mg of TiO₂ (P25) were spread on the bottom of a specially designed quartz plate and placed inside the reaction chamber. In measurements where H₂O needed to be present, the selected gas mixture (pure He, 1.5% CO₂ in He, or 1% H₂) passed through a saturator set at 5 °C (calculated H₂O concentration: 6,000 ppm) before entering the reaction chamber.

Acknowledgements

This work was funded by the German Ministry of Education and Research (BMBF) within the scope of the projects PROPHECY (FKZ: 033RC003) and PRODIGY (FKZ: 033RC024). Prof. Malte Brasholz, University of Rostock, is acknowledged for fruitful discussions. The authors would like to thank Dr. H. Lund (LIKAT) for the collection of the XRD data. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ reduction · heterogeneous catalysis · oxidation half reaction · photocatalysis · reaction mechanism

- [1] a) M. Halmann, *Nature* **1978**, *275*, 115–116; b) T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637–638.
- [2] a) S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408; *Angew. Chem.* **2013**, *125*, 7516–7557; b) J. Rossmesl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J. K. Nørskov, *J. Electroanal. Chem.* **2007**, *607*, 83–89.
- [3] M. Dilla, A. Jakubowski, S. Ristig, J. Strunk, *Phys. Chem. Chem. Phys.* **2019**, *21*, 15949–15957.
- [4] a) B. Mei, A. Pougín, J. Strunk, *J. Catal.* **2013**, *306*, 184–189; b) A. Pougín, M. Dilla, J. Strunk, *Phys. Chem. Chem. Phys.* **2016**, *18*, 10809–10817; c) M. Dilla, A. Pougín, J. Strunk, *J. Energy Chem.* **2017**, *26*, 277–283.
- [5] a) Y. Wang, J. Zhao, T. Wang, Y. Li, X. Li, J. Yin, C. Wang, *J. Catal.* **2016**, *337*, 293–302; b) K. Li, P. Bosi, T. Peng, *ACS Catal.* **2016**, *6*, 7485–7527; c) M. Tahir, B. Tahir, N. A. S. Amin, *Appl. Catal. B* **2017**, *204*, 548–560; d) M. Ye, X. Wang, E. Liu, J. Ye, D. Wang, *ChemSusChem* **2018**, *11*, 1606–1611; e) X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.* **2019**, *119*, 3962–4179.
- [6] I. A. Shkrob, T. W. Marin, H. He, P. Zapol, *J. Phys. Chem. C* **2012**, *116*, 9450–9460.
- [7] M. Dilla, N. G. Moustakas, A. E. Becerikli, T. Peppel, A. Springer, R-Schlögl, J. Strunk, S. Ristig, *Phys. Chem. Chem. Phys.* **2019**, *21*, 13144–13150.

- [8] Y. Yan, W. Shi, W. Peng, Y. Lin, C. Zhang, L. Li, Y. Sun, H. Ju, J. Zhu, W. Ma, J. Zhao, *Commun. Chem.* **2019**, *2*, 88.
- [9] a) L. Liu, H. Zhao, J. M. Andion, Y. Li, *ACS Catal.* **2012**, *2*, 1817–1828; b) L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang, Y. Li, *ACS Catal.* **2016**, *6*, 1097–1108; c) G. Yin, X. Huang, T. Chen, W. Zhao, Q. Bi, J. Xu, Y. Han, F. Huang, *ACS Catal.* **2018**, *8*, 1009–1017; d) J. Gao, Q. Shen, R. Guan, J. Xue, X. Liu, H. Jia, Q. Li, Y. Wu, *J. CO₂ Util.* **2020**, *35*, 205–215.
- [10] M. Dilla, A. Mateblowski, S. Ristig, J. Strunk, *ChemCatChem* **2017**, *9*, 4345–4352.
- [11] M. A. Bañares, I.E. Wachs, *J. Raman Spectrosc.* **2002**, *33*, 359–380.
- [12] R. S. Smith, Z. Li, L. Chen, Z. Dohnalek, B. D. Kay, *J. Phys. Chem. B* **2014**, *118*, 8054–8061.
- [13] N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He, P. Zapol, *J. Am. Chem.* **2011**, *133*, 3964–3971.

Manuscript received: August 25, 2021

Accepted manuscript online: November 12, 2021

Version of record online: November 24, 2021