

# Activation of very stable molecules (CO<sub>2</sub>, N<sub>2</sub>) with catalysis, heat, and light

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## Abstract

For more than half a century, intense research has been conducted on photocatalytic reactions such as water splitting, reduction of CO<sub>2</sub>, or organic synthesis. However, for such reactions at room temperatures, progress is limited, and product yields often do not exceed the millimolar range. In this talk it will be demonstrated that the activation of small, very stable molecules such as CO<sub>2</sub> and N<sub>2</sub>, might be more successful by a combination of catalysis, light and heat. In addition, reliable and reproducible research methodologies are proposed for streamlined progress in photo(thermal)catalysis research.

In the past 14 years, in successive research efforts, we have unraveled many mechanistic details in the reaction progress for the case of TiO<sub>2</sub> P25, using our standardized high-purity gas-phase photoreactor [1] and IR spectroscopy [2]. The main product CH<sub>4</sub> can only be formed via a pathway involving C<sub>2</sub> intermediates such as acetic acid or acetaldehyde, whereas a C<sub>1</sub> mechanism can only lead to CO formation [3]. Light strongly influences already the adsorption of CO<sub>2</sub> as likely first elementary step [2]. Although the formation of carbon-containing products clearly proceeds from CO<sub>2</sub>, oxygen does not evolve but is stored in the TiO<sub>2</sub> bulk. Modification of TiO<sub>2</sub> with an oxygen-evolving co-catalyst leads to a photocatalyst capable of overall water splitting in a gas-solid system, but no carbon-containing products are formed [4]. The reaction pathway from CO<sub>2</sub> to CH<sub>4</sub> is, surprisingly, not a subsequent chain of reduction event, but also involves photogenerated holes [5], so both half reactions are inseparable on TiO<sub>2</sub>. In conclusion, new material combinations such as Z schemes are needed to properly separate the half reactions [6]. Furthermore, instead of pure photocatalytic reactions at room temperature, it is proposed to conduct combined photo- and thermal catalytic reactions. For the latter case, promising results are obtained with industrial-type Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts [7].

In related research efforts, we aim to produce nitric acid “from thin air”, i.e., directly from N<sub>2</sub> and O<sub>2</sub>. Using a Pd/TiO<sub>2</sub> catalyst, the formation of nitrates on the photocatalyst surface at 150°C and irradiation with 365 nm light is observed with IR spectroscopy to understand the reaction pathway and to reduce persistent activation barriers [8].

[1] N.G. Moustakas et al., *Hardware X* **15** (2023) e00448. [2] P. Naliwajko, N.G. Moustakas et al., *Phys. Chem. Chem. Phys.* Accepted Article; [3] A. Pougin et al. *Phys. Chem. Chem. Phys.* **18** (2016) 10809; [4] M. Dilla et al. *Phys. Chem. Chem. Phys.* **21** (2019) 15949; [5] N.G. Moustakas et al., *Chem. Eur. J.* **27** (2021) 17213; [6] A. Hezam et al., *Small Methods* **7** (2023) 2201103; [7] J. Huang, M. Rehner, J. Strunk et al., to be published; [8] M. Gutgesell, A. Zaim, J.Z. Bloh, J. Strunk, to be published.