Determining the CO_2 Photoreduction Mechanism over TiO_2 Surfaces using Density Functional Theory

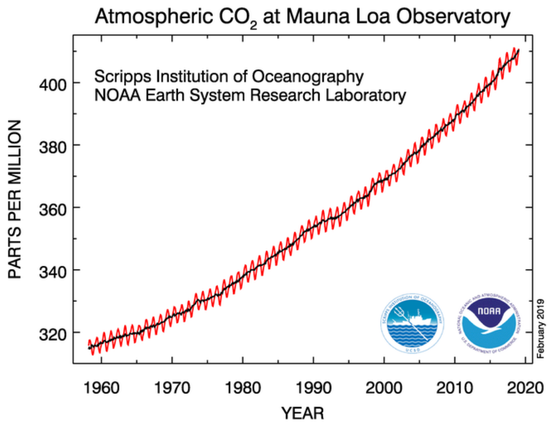
Oskar Cheong[1,*], Thang Pham[2], Piotr M. Kowalski[1], Michael H. Eikerling[1], Aaron Deskins[2]

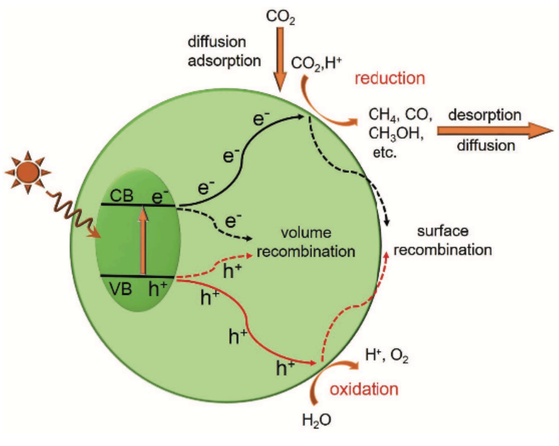
[1]Modeling and Simulation of Materials in Energy Technology (IEK-13), Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52425 Jülich, Germany; [2]Chemical Engineering Department, Worcester Polytechnic Institute, Massachusetts 01609, United States. **Corresponding Author: Oskar Cheong (email: o.cheong@fz-juelich.de)**

With increasing energy demands and continuously rising CO_2 emissions, photocatalytic reduction of CO_2 seems to be a promising way to tackle these issues. Modern computational methods can be utilized to understand, characterize, and predict how catalyst materials could enable the CO_2 reduction reaction. Computational methods can be used to predict which materials may be good catalysts for CO_2 reduction or how such catalysts work on the atomic level. CO_2 reduction mechanisms over TiO_2 have been proposed [1,2], but no definitive mechanism has been determined. The (101) surface is the most stable surface of TiO_2 anatase, but other surfaces may also be highly reactive for CO_2 reduction [3,4]. In this work we modeled the different elementary steps that may occur during CO_2 reduction over different TiO_2 surfaces: anatase (101), anatase (103,100) and rutile (110) surface. The goal of this work is to gain valuable insight on what types of TiO_2 crystals with desired surfaces should be synthesized for efficient CO_2 reduction. We observed the superiority of the formaldehyde pathway over the other pathways for all TiO_2 surfaces. In terms of the efficiency of the CO_2 reduction to CH_4 along the formaldehyde pathway and the CO_2 activation process, the anatase (101) and (100) surfaces showed a much more favorable mechanism towards the formation of CH_4 compared to the other surfaces. Anatase (103) and rutile (110) both experienced high endothermic reaction energies during CO_2 activation. Our results provided valuable insight on what types of TiO_2 crystals with desired surfaces should be synthesized for efficient CO_2 reduction.

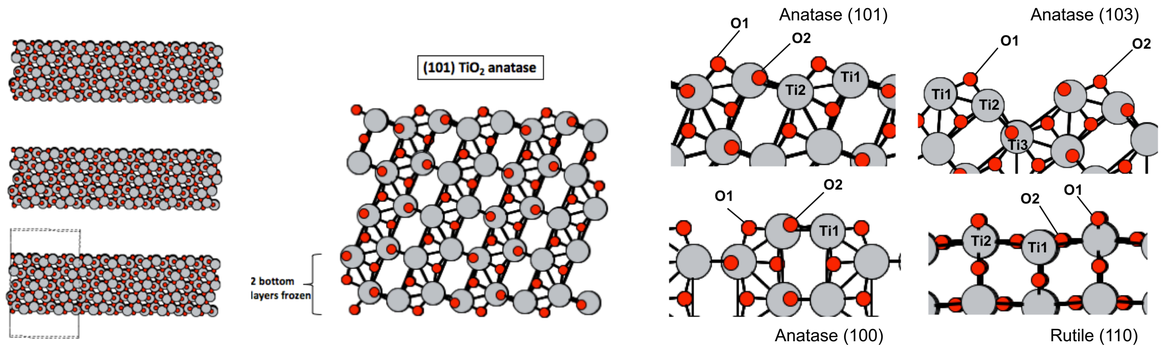
CO_2 as the global problem

While it is known that CO_2 emissions have become a global issue, most research in tackling the CO_2 problem have been done in the areas of mitigating or storing this greenhouse gas. However, another emerging approach is using photocatalyst to "recycle" CO_2 and reduce it to value-added products such as CH_4.



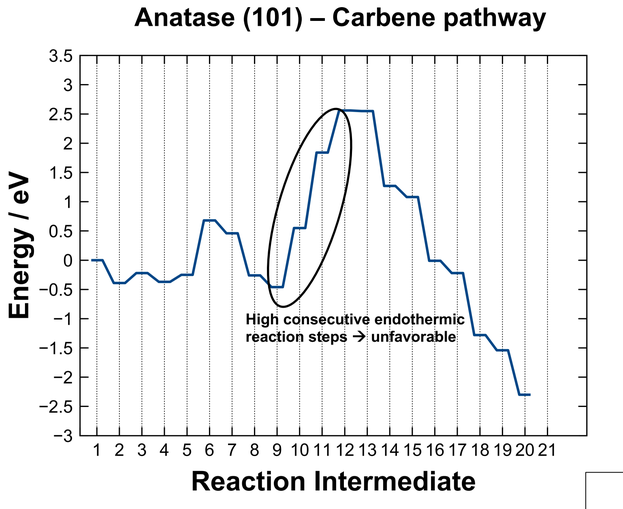


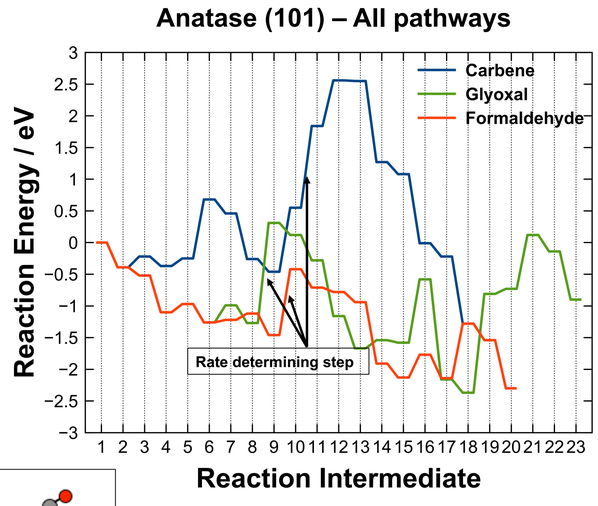
TiO_2 as a suitable CO_2 photocatalyst



TiO_2 is considered the benchmark photocatalyst for CO_2 photoreduction due to its stability, cost and non-toxicity. CO_2 reduction reaction mechanism towards CH_4 is still debatable. Carbene, formaldehyde and glyoxal pathways (named after their intermediates) have been proposed. In this work we wanted to answer the question of what pathway is the most favorable one on each TiO_2 surface and whether the pathway is independent of the surface.

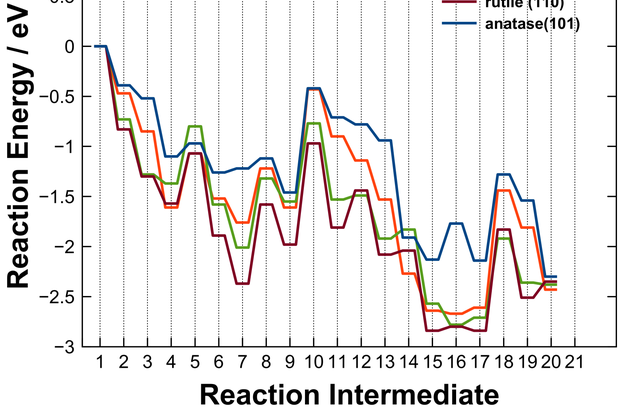
Pathway analysis





Pathway	Rate determining step	Energy [eV]
Carbene	C + H_2O (11)	1.29
Formaldehyde	H_2CO (10)	1.05
Glyoxal	OCHCHO (9)	1.58

- **Formaldehyde pathway is most favorable** in case of anatase (101) surface → in good agreement with literature
- **Is the trend similar for the other surfaces?**

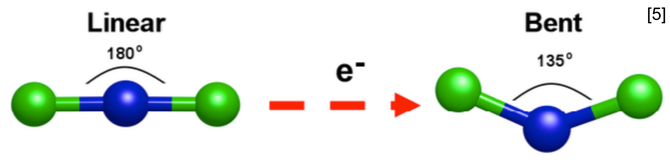


- Similar trend for other surfaces compared to anatase (101) surface, HCOOH is a possible byproduct in the case of other surfaces. Cause: the adsorption energy of H is weaker on anatase (101) surface
- Rutile (110) shows more endothermic steps → less photocatalytic active

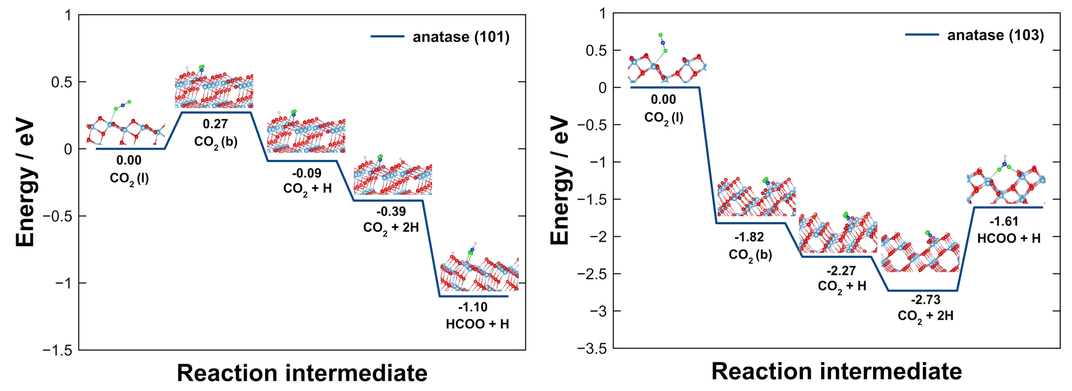
Surface	Adsorption Energy [eV]
Anatase (101)	-2.64
Anatase (103)	-3.18
Anatase (100)	-3.09
Rutile (110)	-3.36

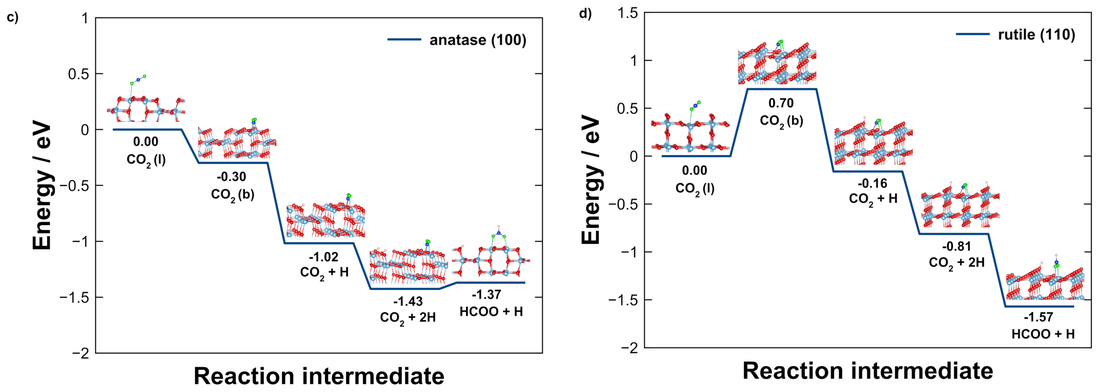
Adsorption energy of H on TiO_2 surface

CO_2 Activation



- CO_2 activation believed to be first step during CO_2 reduction
- We have to take into account linear to bent CO_2 transformation





- **Anatase (101) and anatase (100) have lower rate determining steps**
- **CO_2 activation has an impact on different surface terminations**

Results and Outlook

- Results: Reference anatase (101) surface and anatase (100) surface most favorable for CO_2 reduction towards CH_4, taking into account CO_2 activation
- Outlook: Experimental validation, calculation of transition states, CO_2 reduction on brookite crystal

Acknowledgement: We acknowledge having access to JARA-HPC partition.

References:

[1] Chung Man Ip and Alessandro Troisi. A computational study of the competing reaction mechanisms of the photo-catalytic reduction of CO2 on anatase(101). Physical Chemistry Chemical Physics, 18, 2016.
[2] Yongfei Ji and Yi Luo. Theoretical study on the mechanism of photoreduction of CO2 to CH4 on the anatase TiO2(101) surface. ACS Catalysis, 6:2018–2025, 2016.
[3] Ci Zhang Wen, Hai Bo Jiang, Shi Zhang Qiao, Hua Gui Yang, and Gao Qing Lu. Synthesis of high-reactive facets dominated anatase TiO2. Journal of Materials Chemistry, 20, 2011.
[4] Kunat, M., Traeger, F., Silber, D., Qiu, H., Wang, Y., van Veen, A. C., Woell, Ch., Kowalski, P. M., Meyer, B., Haettig, C. & Marx, D. "Formation of weakly bound, ordered adlayers of CO on rutile TiO2(110): A combined experimental and theoretical study", J. Chem. Phys., 130, 144703, 2009.
[5] Junbo Chen. Effect of defects and photoexcited electrons on CO2 reduction using supported single atom catalysts. June 2018.