

P3.6 Photocatalytic generation of oxalate under high-purity conditions

Topic and overall goal. The photocatalytic CO₂ reduction to hydrocarbon fuels is a highly promising energy conversion (solar-to-chemical) process. As CO₂ is a thermodynamically very stable molecule ($\Delta G^\circ = -394 \text{ kJ mol}^{-1}$), any carbon-based impurity present in a photoreactor, is likely to react first leading to the formation of carbonaceous products, falsely attributed to performance of the photocatalyst.¹ A reactor constructed for and operated under high-purity conditions is critical to collect reproducible data and reach reliable conclusions.² Especially for the formation of oxalate using TM based systems previous studies showed that impurities can lead to misinterpretation of the catalytic data. We would like to address this important question using a customised reaction setup for the study of photocatalytic CO₂ coupling under high-purity conditions.

Specific aims and work plan. All photocatalytically active molecular systems developed in P3.1-3.4 will be studied for light-driven coupling of CO₂ under high-purity conditions. An available customised reaction setup (Figure P3.6) will be modified to accommodate the respective reaction conditions, in particular a liquid phase. Of note, this methodology can be applied in a wider range of reaction systems being investigated. An approach that uses ionic liquids as solvents is highly desirable to ensure high-purity conditions within the photoreactor systems while investigating the gas and solution phase on-line. Crucial parameters can be addressed, such as influence of light sources (spectral range, intensity), temperature (up to 150 °C) and gas phase compositions (reactant concentration and partial pressures). Analysis of product formation in the gas phase is done using a gas chromatograph equipped with flame ionization detector and a barrier discharge ionization detector that allow the identification and quantification of reactants and here undesirable gaseous byproducts (H₂O, CO₂, O₂, and C₁-C₁₄ hydrocarbons compounds) down to the 1 ppm range. For H₂ and CO the limit was identified to be 20 ppm at atmospheric pressure. The liquid phase, desirably an ionic liquid system (e.g., 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide (BMIm)[NTf₂]), is analyzed by means of liquid chromatography (e.g., HPLC or LC-MS), NMR techniques (e.g., oxalic acid: ¹³C 162.3 ppm; methyl oxalate: ¹³C 158.1, 53.6 ppm; (BMIm)[NTf₂]: ¹³C 115-140, 10-50 ppm), or FTIR measurements.

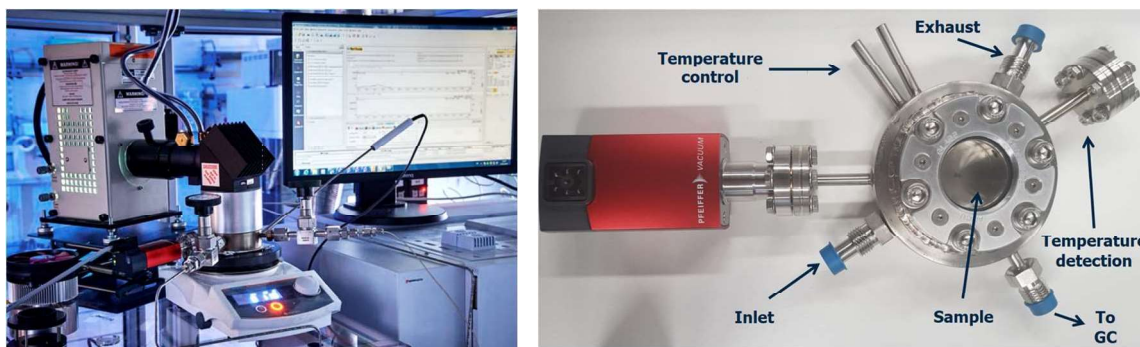


Figure P3.6. High-purity photoreactor setup (left) and details of the photoreactor chamber (right).

Within this project the PhD student will receive training in the operation of photocatalytic conditions under high-purity conditions and accurate analysis of reactant consumption and product formation using various analytical techniques. The student will acquire expertise in the field of reaction engineering, photocatalysis and analytical chemistry.

Connection within the RTG. This PhD project will be jointly supervised by Jennifer Strunk and Axel Schulz. Within the RTG there will be a close collaboration with the Pospech (organic photocatalysis), Lochbrunner (pump-probe spectroscopy of photoredox and light-switchable biradical metal catalysts) and Bokareva group (computational analysis).

1 N. G. Moustakas, J. Strunk, *Chem. Eur. J.* **2018**, 24, 12739-12746.

2 a) A. Pougin, M. Dilla, J. Strunk, *Phys. Chem. Chem. Phys.* **2016**, 18, 10809-10817; b) DIN SPEC 91457: Photocatalysis – Determination of product formation in CO₂ reduction.