MOFs for Photocatalytic Water Splitting & Carbon Dioxide Conversion

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Executive Summary

The aim of this project was the identification of Metal-Organic framework photocatalysts capable of harnessing solar energy and produce value-added products from CO_2. Our efforts are structured across three interconnected work packages (WPs) that synergistically integrate computational and experimental approaches.

WP1. Building a database for catalytically active MOFs. We developed automated algorithms to screen the Cambridge Structural Database (CSD) MOF subset and identify promising MOF candidates with high conductivity by performing high-throughput density functional theory (DFT) calculations. The DFT results provide a large database of optimised structures for which we calculated the bandgap and the density of states. The analysis of the structure-property relationship demonstrated the effect of the presence of different charge-transport pathways on the electronic properties of MOFs which is crucial for the identification of promising materials for catalytic CO_2 reduction. Through these high-throughput DFT calculations we identified 100 MOFs based on criteria such as porosity (largest cavity diameter > 3 A), band-gap (ca. 0), and DoS Fermi energy (> 0 eln/cell).

WP2. Microkinetic modelling of photocatalytic CO_2 reduction. We developed a microkinetic model to describe the intrinsic kinetics of CO_2 photocatalytic reduction to CO and to formic acid over UiO-66(Zr), as a model MOF. A periodic optimization was conducted to identify a defective cluster model with 6 Zr atoms and 11 linkers. The kinetic parameters governing the process were estimated by conducting cluster calculations using the PBE0 exchange-correlation functional. We built a reaction networks including adsorption, desorption and surface reaction steps, by assuming the presence of two active sites, on the unsaturated metal node and on the organic linker. The model indicates a maximum generation rate of formic acid of 36 μmol/g/h.

WP3. Photocatalytic experiments. We conducted an experimental investigation using a 300 W UV lamp to detect the formation of CO from photocatalytic CO_2 reduction over three exemplary model MOFs, UiO-66, UiO-66-NH_2, and MIL-125. Gaseous samples were collected during the reaction and analysed using a Fourier transform infrared (FTIR) spectrometer. The experiments confirmed the formation of CO over UiO-66 and UiO-66-NH_2 when utilizing both triethanolamine and methanol as sacrificial agents. As part of future work, we will quantify the product species and extend the investigation to additional structures identified through high-throughput screening.