Designing accessible and stable active sites in MOF-based photo/electrocatalysis

Dominik Eder

Institut für Materialchemie, TU Wien, Gertreidemarkt 9/BC, 1060 Wien, Austria
E-mail: dominik.eder@tuwien.ac.at

Abstract

Metal-Organic frameworks (MOFs) have recently gained interest as an innovative class of photocatalytic and electrocatalytic materials owing to catalytically active oxo-metal clusters connected to photoactive organic linkers through a well-ordered micropore network that yields exceptionally high surface areas. In dynamic processes and especially in liquid phase catalysis, the accessibility of active sites becomes a critical parameter as the reactant diffusion is often limited by the inherently small micropores of MOFs.

In this talk, I will present a promising strategy to overcome this challenge. It involves the synthesis of mixed-ligand MOFs, followed by selective ligand removal (SELIRE) upon thermal stimulus to design microporous-mesoporous MOFs [1]. As an example, we synthesized photoactive MOFs of the MIL-125-Ti family with two distinct hierarchical pore architectures resembling either large cavities or branching fractures, both of which significantly improved the photocatalytic hydrogen evolution (HER) rates of the MOFs by up to 500%. In another example, we show that these pores also greatly enhanced the potential of these MOFs to adsorb large molecules, such as glyphosate, from waste water [2]. The enhancements induced by the SELIRE process originate from 1) the formation of new under-coordinated adsorption sites and 2) better access to catalytic sites by facilitating reactant diffusion through the pores.

We will further demonstrate how this mixed-ligand approach can greatly enhance the structural integrity and durability of zeolitic imidazolate frameworks (ZIFs) in water-based environments und applied irradiation and electric fields as well as their conductivity and activity towards (photo)electrocatalytic HER and OER reactions [3,4]. Moreover, we will discuss how the creation of open-metal sites through the SELIRE process affects the rate limiting steps for these reactions [5]. In the last part, we will briefly explore the benefits of photoactive MOFs with 2D-arranged Ti-SBUs (i.e. COK-47 as an example) on facilitating charge separation, transport and extraction to adsorbed reactants [6].

References

[1] Naghdi et al., Nat. Commun. 2022, 13, 282.; [2] Naghdi et al., Adv. Funct. Mater. 2023, 2213862.; [3] Zheao et al.. Small, 2024, 20, 2307981; [4] Zheao et al., Nat. Commun. 2024, 15,1; [5] Zheao et al., Angew. Chem., 2025, 64(7), e202419913; [6] Ayala et al., Adv. Ener. Mater., 2023, 2370133