MOFs for Photocatalytic Water Splitting and Carbon Dioxide Conversion

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Highlights

- Developed an automated algorithms to screen the Cambridge Structural Database (CSD) MOF subset.
- Developed a general computational framework to describe the kinetics of CO_2 reduction at the mechanistic level.

1. Introduction

The development of efficient catalysts which utilize solar energy to convert CO_2 to produce value-added chemicals or fuels is extremely appealing as it can simultaneously reduce the GHG emissions and provide energy storage solutions. In recent years, novel solid catalysts such as metal-organic frameworks (MOFs) have demonstrated great potential in energy conversion systems. In this work, we have developed a systematic multi-scale computational approach to identify outstanding materials from the Cambridge Structure Database (CSD) MOF subset for CO_2 reduction and delineate the roles of surface chemistry and functionalization in governing catalytic activity in MOFs.[1-2] We demonstrate how this computational approach can vastly speed up the design of functional materials with real world impact, and discover new MOFs that can be applied for fuel production via photocatalytic CO_2 reduction processes.

2. Methods

First, we developed an automated algorithms dive into the CSD MOF subset and quickly identify promising MOF chemistries with catalytically active sites; Second, we conducted high-throughput computational screening based on the calculation of the MOFs band gap and ionization potential calculated by density functional theory (DFT) using VASP with LDA and HSE level to predict the electronic properties of the identified MOFs. We developed a detailed microkinetic model by conducting quantum mechanical calculations using Gaussian16 computational chemistry software to optimize reactants, products and transition states. The kinetic constants governing the process were estimated from transition state theory.

3. Results and discussion

We identified MOFs with the band gap falling into the semi-conductivity range, (between 1 and 3 ev), which corresponds to the visible light range of wavelengths. For the CO_2 reduction to take place, the free energy change per electron of the reaction has to match the energy of the excited electron. (i.e. the minimum of the conduction band)[3] **Fig. 1** shows the calculated band gap for some examplary MOFs. **Fig. 2** shows some of the promising MOF structures identified for CO_2 reduction as a result of the high-throughput screening.

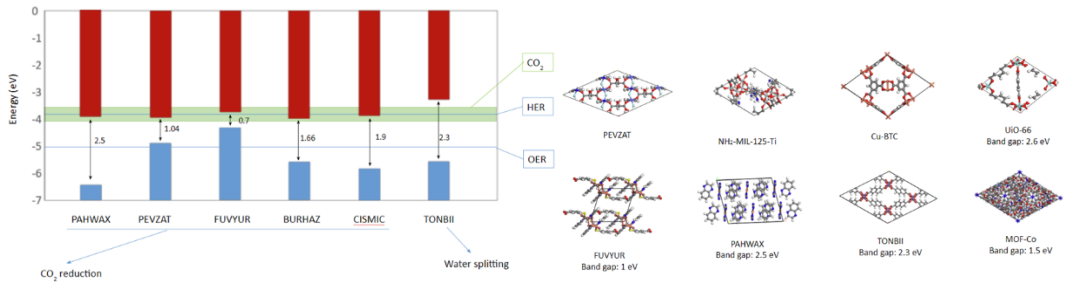


Figure 1. Selection criteria based on VBM (valence band maximum) and CBM (conduction band minimum). Red: conduction bands, Blue: valence band, HER: hydrogen evolution reaction, OER: oxygen evolution reaction.

Figure 2. Promising structures identified for CO_2 reduction

Then we applied binding energy calculations on best performing candidates, a reaction coordinate diagram for the UiO-66 framework was constructed (**Fig. 3**). The relative thermal enthalpies for each elementary step in the whole reaction network are shown in Fig.6. This analysis allowed for the calculation of the rate coefficients needed for the development of the micro-kinetic model.

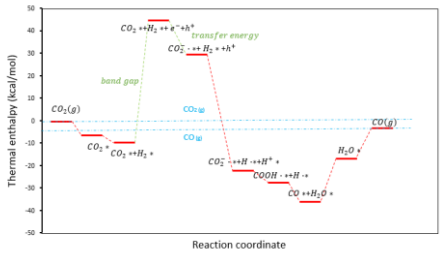
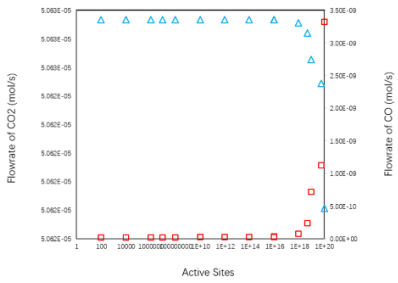


Fig. 3. Reaction coordinate diagram showing the reaction thermal enthalpies. Red dashed lines show the main reaction pathway, blue dashed lines show the thermal enthalpy level of CO_2 and CO in the gas phase.

Fig. 4 shows the simulated CO_2 and CO molar profiles, as a function of the number of active sites in the reactor.



4. Conclusions

We have developed automated algorithms to screen the Cambridge Structural Database (CSD) MOF subset and identify promising MOF chemistries and candidates with high conductivity by performing high-throughput density functional theory (DFT) calculations. We have developed a general computational framework to describe the kinetics of CO_2 reduction at the mechanistic level. Rate coefficient were obtained for UiO-66 and UiO-66-NH_2 to describe the formation of CO and HCOOH.

References

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Keywords
MOF; Photocatalysis; High-throughput screening; Kinetic modelling;