

Visit CMM- Utrecht

September 10, 2018

Visitors from CMM

Simon Bailleul

Chiara Caratelli

Dr. Julianna Hajek

Pieter Cnudde

Dr. Sven Rogge

Dr. Louis Vanduyfhuys

Sander Borgmans

Dr. Francesco Muniz Miranda

Grand Challenge 1: Modeling that accounts for operating conditions (temperature, pressure and solvent)

Presentation 1 : Sander Borgmans – Sven Rogge – Louis Vanduyfhuys (15 minutes)

Probing the mechanical, thermal, and chemical stability of MOFs and COFs

While nanoporous materials such as metal-organic framework (MOFs) and covalent organic frameworks (COFs) often exhibit unprecedented porosities that make them attractive for applications such as gas adsorption and heterogeneous catalysis, the large voids inside these materials may also limit their mechanical, thermal, and chemical stability. To further promote MOFs and COFs towards functional devices, it is therefore fundamental to understand from a microscopic point of view how the stability of these materials can be affected by local alterations in their framework structure. Here, we investigate how the mechanical stability of these materials can be probed computationally, both near equilibrium and near mechanical instability. Furthermore, we provide an overview of those factors influencing the stability of MOFs and COFs, focusing on isovalent substitutions, the introduction of functional groups, or the presence of local defects.¹⁻⁴ Moreover, we also demonstrate how this procedure can be extended to also model the thermal and chemical stabilities of these materials.^{5,6}

Presentation 2 : Chiara Caratelli – Julianna Hajek

Effect of solvent on UiO-66

Within this contribution we emphasize the nanoscopic effects of solvents embedded in the stable and rigid UiO-66 metal organic framework. We observe a dynamic effect on the solvent on the active sites, and an evolution of their topology which cannot be tracked by static calculations. Supramolecular structures formed by a network of hydrogen bonds are observed in both methanol and water solvent. Protons and other ions can be transported to and from the active sites. The positive charge of the ions is stabilized by the solvent, which could be crucial in stabilizing charged reaction intermediates. The acidic dissociation constants were estimated for the protons of the active sites and on the pristine brick by means of novel advanced MD methods. These calculations, which include all the interactions with the solvent, are much more accurate than the comparison of probe molecule adsorption energies, but

more computationally demanding. *It would be interesting to start a discussion on how to track experimentally the bond rearrangements in the neighborhood of the active sites, and how they connect to the proton acidity.*^{7,8}

Presentation 3 : Pieter Cnudde

Effect of temperature on the nature of catalytic cracking intermediates

Within this presentation we show how intermediates observed during catalytic cracking of alkenes over zeolites may change depending on the operating conditions and more in particular in terms of temperature. Catalytic cracking of alkenes takes place at elevated temperatures in the order of 773–833 K. By using a complementary set of modeling techniques we show that the occurrence of alkoxides, carbenium ions and π -complexes may change and also critically depends on the degree of branching and length of the alkene. We would like to initiate a discussion with the experimentalists on how to obtain spectroscopic information on the nature of elusive intermediates at operating conditions.^{9,10}

Grand Challenge 2: Modeling that account for different types of spatial heterogeneity

Presentation 4 : Simon Bailleul

Characterization of zeolites modified with metals

There is a growing awareness that complex chemical transformations with emphasis on high selectivity, long catalyst lifetimes require well defined active sites which can potentially cooperate or be tuned to achieve the desired structure-activity relationships. Herein we show some concepts required to model such extended active sites which are characterized by spatial heterogeneities. One of the main challenges from theory is how to obtain experimental information on the nature of the active site. We would like to initiate a discussion with experimentalists on potential input via spectroscopic techniques that enable detailed insight into the position and the nature of metal embedding in zeolites. As a special case study the presence of extra framework aluminum species can be considered.^{11,12}

Presentation 5 : Sander Borgmans – Sven Rogge

Understanding crystalline heterogeneity in MOFs and COFs

The concept of reticular synthesis has enabled the rational design of crystalline framework materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) by judiciously combining appropriate molecular building blocks into a predetermined topology. Experimentally, however, this concept requires strong directed bonds between rigid building blocks as well as a largely reversible crystallization process, to arrive at well-defined, ordered structures with atomic precision. When the crystallization reaction is not sufficiently reversible, the material cannot correct for defects occurring during crystallization, affecting the growth and crystallite sizes and leading to spatially heterogeneous materials. Here, we explore both theoretically and experimentally how powder X-ray

diffraction (PXRD) patterns allow to probe the crystalline heterogeneity of the material, and distinguish whether multiple phases may coexist within the material [1]. Furthermore, we present from a computational point of view how we anticipate to tackle spatial heterogeneity at length scales of several tens of nanometers, which are inaccessible in current atomistic simulations. This would for instance allow to dynamically assess the formation and separation of different phases in these framework materials. To this end, we would like to open the discussion on how possible crystalline and amorphous regions inside these framework materials can be characterized experimentally as input and validation of the theoretical procedure.¹³

Grand Challenge 3: Modeling accounting for the evolution of the materials within in time (finite lifetime)

Presentation 6 : Louis Vanduyfhuys

Regeneration of soft porous crystals undergoing irreversible phase transitions

Soft porous crystals possess a network with long-range structural order, but are also flexible as they can transform between various states upon external stimuli such as pressure, temperature and guest adsorption. We have developed a generalized thermodynamic framework to construct the underlying Helmholtz free energy as function of the state variables that govern the observed behavior based on microscopic simulations. Such models reveal that depending on the type of free energy profile, the transition may be irreversible, meaning that once the forward transition has occurred and the stimulus is removed, the material does not return to its original state. Such irreversibility severely limits the applications as there is no possibility for a cyclic process. Therefore, we aim to explore the response of these materials as function of multiple stimuli in order to find efficient pathways to regenerate soft porous crystals and return them to their initial state. Proof of concept examples will be shown to demonstrate how one can achieve such regeneration using temperature and competitive guest adsorption.⁶

Presentation 7 : Francesco Muniz Miranda

Computational UV-Vis spectroscopy

How accurate and for which systems can we calculate UV-Vis spectra today? UV-Vis spectra are used as a powerful tool to characterize various processes. The calculation of these spectra involves knowledge of the electronic excited states and their orbital character, and within this presentation, we will show for which systems UV-Vis spectra can nowadays be calculated with reasonable accuracy. Particular challenges are still faced to calculate UV-Vis spectra in complex molecular environments, such as complexes embedded in a nanoporous environment or within a solvent. Furthermore, calculation of UV-Vis spectra of high spin complexes is still challenging. Within this talk we would like to initiate a discussion with the experimentalists to obtain good benchmark systems for theoreticians to further progress the field for the calculation of properties dependent on the excited states of complex molecular systems.

1. S. M. J. Rogge, L. Vanduyfhuys, A. Ghysels, M. Waroquier, T. Verstraelen, G. Maurin and V. Van Speybroeck, *J. Chem. Theory Comput.*, 2015, **11**, 5583-5597.
2. S. M. J. Rogge, J. Wieme, L. Vanduyfhuys, S. Vandenbrande, G. Maurin, T. Verstraelen, M. Waroquier and V. Van Speybroeck, *Chemistry of Materials*, 2016, **28**, 5721-5732.
3. S. M. J. Rogge, M. Waroquier and V. Van Speybroeck, *Accounts Chem. Res.*, 2018, **51**, 138-148.
4. S. M. J. Rogge, S. Caroes, R. Demuynck, M. Waroquier, V. Van Speybroeck and A. Ghysels, *J. Chem. Theory Comput.*, 2018, **14**, 1186-1197.
5. R. Demuynck, S. M. J. Rogge, L. Vanduyfhuys, J. Wieme, M. Waroquier and V. Van Speybroeck, *J. Chem. Theory Comput.*, 2017, **13**, 5861-5873.
6. L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier and V. Van Speybroeck, *Nat. Commun.*, 2018, **9**, 9.
7. J. Hajek, C. Caratelli, R. Demuynck, K. De Wispelaere, L. Vanduyfhuys, M. Waroquier and V. Van Speybroeck, *Chem. Sci.*, 2018, **9**, 2723-2732.
8. C. Caratelli, J. Hajek, S. M. J. Rogge, S. Vandenbrande, E. J. Meijer, M. Waroquier and V. Van Speybroeck, *Chemphyschem*, 2018, **19**, 420-429.
9. P. Cnudde, K. De Wispelaere, J. Van der Mynsbrugge, M. Waroquier and V. Van Speybroeck, *J. Catal.*, 2017, **345**, 53-69.
10. J. Hajek, J. Van der Mynsbrugge, K. De Wispelaere, P. Cnudde, L. Vanduyfhuys, M. Waroquier and V. Van Speybroeck, *J. Catal.*, 2016, **340**, 227-235.
11. I. Yarulina, S. Bailleul, A. Pustovarenko, J. R. Martinez, K. De Wispelaere, J. Hajek, B. M. Weckhuysen, K. Houben, M. Baldus, V. Van Speybroeck, F. Kapteijn and J. Gascon, *Chemcatchem*, 2016, **8**, 3057-3063.
12. I. Yarulina, K. De Wispelaere, S. Bailleul, J. Goetze, M. Radersma, E. Abou-Hamad, I. Vollmer, M. Goesten, B. Mezari, E. J. M. Hensen, J. S. Martinez-Espin, M. Morten, S. Mitchell, J. Perez-Ramirez, U. Olsbye, B. M. Weckhuysen, V. Van Speybroeck, F. Kapteijn and J. Gascon, *Nat. Chem.*, 2018, **10**, 804-812.
13. M. J. Cliffe, W. Wan, X. D. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F. X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 8.