Operando modelling of the dynamic behaviour of Metal Organic Frameworks

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During the last two decades, metal-organic frameworks (MOFs) have evolved towards one of the most intriguing materials of current science, thanks to their versatile nature being composed of inorganic and organic building blocks and their ability to be tuned towards high-tech applications [1]. A huge number of MOFs have been synthesized, but the true challenge consists in designing materials with the desired functional behavior. Furthermore it is important to account that the function is highly dependent on the operating conditions. Within this talk, I will address how molecular modeling at operating conditions, in close synergy with experimental observations, plays a pivotal role to meet this challenge.

Due to their hybrid nature, modeling MOFs requires simulation techniques at the crossroad of molecular and solid-state modeling [2,3,4]. Furthermore, the materials possess inherent defects and structural disorder, which may be exploited for beneficial purposes, but which may also compromise the stability of the materials [5,6]. To obtain molecular level insight into this intriguing and inherently dynamic behavior, an ingenious combination of ab initio based and force field-based methods as well as thermodynamic models are required. To properly model the dynamic behavior of MOFs, it is essential to mimic experimental conditions as closely as possible. To this end we try to map the free energy surface at operating conditions using enhanced sampling molecular dynamics simulations. The dynamic behavior may be related to the flexible behavior of the framework upon external triggers such as temperature, mechanical pressure or adsorption [7,8,9], but also an intrinsic dynamic flexibility related to changes in the coordination numbers may occur upon adsorption or activation [6]. The latter is especially important to create active sites for catalysis [4,10]. Within this talk, I will show how advanced sampling techniques may be used to assess phenomena taking place at various time scales and to follow in situ and operando the molecular behavior of the materials. During this talk, I will illustrate with various case studies, which were performed in close synergy with experimentalists, how the rich computational toolbox may help to unravel the properties and intriguing dynamic behavior of MOFs.

[1] H. Furukawa, K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, Science 341: 123044, 2013

[2] S. O. Odoh, C. J. Cramer, D. G. Truhlar, and L. Gagliardi, Chem. Rev. 115: 6051, 2015

[3] F.-X. Coudert and A. H. Fuchs, Coord. Chem. Rev. 307: 211, 2016

[4] S. M. J. Rogge, A. Bavykina, J. Hajek, et al., Chem. Soc. Rev. 46: 3134, 2017

[5] S. M. J. Rogge, J. Wieme, L. Vanduyfhuys, S. Vandenbrande, G. Maurin, T. Verstraelen, M. Waroquier, and V. Van Speybroeck, Chem. Mater. 28: 5721, 2016

[6] J. Hajek, C. Caratelli, R. Demuynck, K. De Wispelaere, L. Vanduyfhuys, M. Waroquier, and V. Van Speybroeck, Chem. Sci. 9: 2723, 2018

[7] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, and R. A. Fischer, Chem. Soc. Rev. 43: 6062, 2014

[8] L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, and V. Van Speybroeck, Nat. Commun. 9: 204, 2018

[9] J. Wieme, K. Lejaeghere, G. Kresse, V. Van Speybroeck, Nat. Commun. 9: 4899 , 2018

[10] C. Caratelli, J. Hajek, F. G. Cirujano, M. Waroquier, F. X. Llabrés I Xamena, and V. Van Speybroeck, J. Catal. 352: 401, 2017

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