Dynamic interplay between defective UiO-66 and confined solvent: insights into a reaction environment at operating conditions

C. Caratelli, Center for Molecular Modeling, Ghent University
J. Hajek, S.M.J. Rogge, A. Lamaire, M. Waroquier, V. Van Speybroeck, Center for Molecular Modeling, Ghent University

UiO-66, composed by Zr-oxide bricks and terephthalate linkers, is currently one of the most studied metal organic frameworks due to its exceptional stability that allows the presence of structural defects. The undercoordinated Zr atoms on the defect sites are responsible for the catalytic activity of the material. When a solvent is present, defect coordinating species can introduce additional Brønsted sites that can have a key role in reactions. Moreover, the material, though exceptionally stable, has been shown to be more dynamic than originally anticipated, allowing rearrangement of the linkers around the bricks that lead to linker exchange and formation of defects in a solvent. So far nanoscopic insight into the dynamic formation of active sites at operating conditions in presence of a confined solvent are still missing. Herein, a multilevel modeling approach for the defective UiO-66 material is presented based on ab initio molecular dynamics simulations at realistic conditions with a full loading of methanol and water solvent in the pores of the material. The behavior of a liquid can undergo drastic changes when confined into pores of molecular size, and in the case of UiO-66, vibrational density of state and radial distribution functions show that it can be rationalized as a combination of two opposing factors. On the one hand, the interaction between organic linkers and solvent is dominated by hydrophobic effects that confine the solvent in the pores. On the other, the bricks offer hydrophilic Brønsted acid sites that support and interact via hydrogen bonds with the solvent. Moreover, on the defective sites, the solvent strongly interacts with the Zr atoms. To gain quantitative knowledge of the strength of these interactions, the coordination between solvent and Zr was further investigated by means of metadynamics simulations. The simulations show that, though strongly bonded, water molecules can decoordinate from the Zr atom at standard conditions, to open the site for catalysis. Moreover, additional water molecules can be adsorbed, generating an overcoordination of the Zr atom, which leads to a partial decoordination of a linker. This interplay between solvent and material could be the key to explain the dynamic effects that lead to linker exchange and defect formation, and this is the first time that it has been computationally modeled at operating conditions. These findings shed light on the exceptional dynamic stability of the defective UiO-66 material and its dynamic interactions with protic solvents during postsynthetic treatment.

Representation of water solvent in the pores. Left - hydrogen bond network. Middle - water molecules in proximity of the active sites. Right - water molecules that do not interact with Zr atoms.


E-mail: chiara.caratelli@ugent.be