Long time dynamics from short time simulations

March 12, 2014 to March 14, 2014

Location : CECAM-Lugano, Lugano, Switzerland
Logistics Lugano
Public Transport

Active site engineering of Metal-Organic-Frameworks guided by molecular modeling

Matthias Vandichel
Center for Molecular Modeling, Ghent University, Belgium

Coauthor(s) : Samuel Moors[1] AND Frederik Vermoortele[2] AND Dirk De Vos[2] AND Michel Waroquier[1] AND Veronique Van Speybroeck[1]
[2] Centre for Surface Chemistry and Catalysis, University of Leuven, Belgium

Abstract

Metal-Organic Frameworks (MOFs) are porous crystals, composed of interconnecting inorganic and organic moieties. As the metals are highly dispersed in the framework, they attract increasing interest in heterogeneous catalysis. Apart from the stability issues of these MOFs, it is not always clear what the active sites are and how they can catalyze reactions. In this contribution, we will focus on UiO-67 (UiO = material of the University of Oslo) type materials, in which substituted biphenyldicarboxylate linkers are connected with inorganic [Zr6O4(OH)4]12- bricks. The Zirconium sites – according to the experimentally refined crystal structure – are fully saturated and not accessible, meaning that defects (or missing organic linkers) need to be present in order to make the Zr sites catalytically active. Very recently, we already have postulated and found such active sites in similar MOFs (UiO-66 type) [1,2]. Furthermore, we showed that the activity of these MOFs could be modulated by using substituted linkers [1] and that the amount of active sites could be drastically increased with the addition of mono-carboxylic acid during the synthesis, followed by a procedure to remove these acids [2]. As a clever choice of the substituent positions in the UiO-67 type materials leads to well defined active sites, a further computational study on these materials will lead to a better understanding of the substituent effect.

We studied the catalytic activity of the UiO-67 type materials with the citronellal cyclization. This reaction is studied via a 2D-metadynamics simulation (NPT ensemble) which confirms the concerted nature of the cyclization reaction. Furthermore, our initial results show that the substituent effect is clearly visible in the free energy barriers. Detailed analysis of the metadynamics trajectories and the free free energy surface reveal both steric and energetic effects of the substituent groups. The obtained computational results will also be verified with experimental results in the future.

References

[1] F. Vermoortele, M. Vandichel, B. Van de Voorde, R. Ameloot, M. Waroquier, V. Van Speybroeck, D.E. De Vos, AngewandteChemie International Edition, 51, 4887 (2012).
[2] F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, D.E. De Vos, Journal of the American Chemical Society 135, 11465 (2013).

Return to list