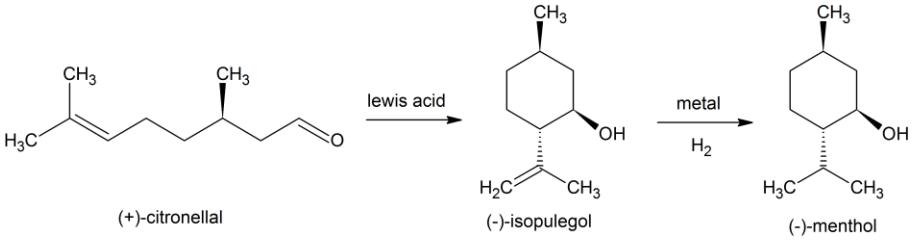
Modeling Lewis catalyzed reactions in Metal Organic Frameworks

Matthias Vandichel,[†] Stijn Cottenie,[†] Frederik Vermoortele,[‡] Dirk De Vos,[‡] Michel Waroquier,[†] Veronique Van Speybroeck,[†]

[†]Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium
[‡]Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, B-3001 Leuven

Recently, the spectrum of nanoporous materials like zeolites and zeotype structures has been further expanded through the discovery of a new class of hybrid porous solids [1]. Those materials, nowadays also known as metal organic frameworks or MOFs, consist of both inorganic and organic moieties. Certain MOFs exhibit a very interesting adsorption and even catalytic behavior [2]. Within this study, we will focus on the modeling of different Lewis acid catalyzed reactions in various MOFs: Cu connected with 1,3,5-benzenetricarboxylate linkers (Cu_3BTC_2) and an $Zr_6O_4(OH)_4$ octahedron connected with (amino-)terephtalate linkers (both UiO-66 and UiO-66(NH_2)). The cyclization of citronellal, already tested experimentally on Cu_3BTC_2 [3], was taken as the first probe reaction. The desired cyclization product is isopulegol, which can be hydrogenated to menthol.



(+)-citronellal (-)-isopulegol (-)-menthol

This selectivity towards isopulegol can be increased by a Brønsted acid treatment of Cu_3BTC_2. The fact that this Brønsted acid has itself a lower selectivity towards isopulegol suggests a dual site catalytic mechanism operative at the modified active sites and offers a excellent opportunity to verify this by molecular modeling. Furthermore, the UiO-66(NH_2) has successfully been applied experimentally for the selective cyclization of citronellal and the Jasmine aldehyde production from benzaldehyde and heptanal.
Within this contribution, possible reaction routes leading to the various isopulegol isomers are studied from theoretical viewpoint on Cu_3BTC_2 and UiO-66. Also, the Jasmine aldehyde production will be discussed on both UiO-66 and UiO-66(NH_2) clusters. The theoretically obtained selectivities on small MOF-clusters could already validate those promising experimental trends. The results are then further refined by taking into account a larger portion of the Metal Organic Framework, as to be representative for the actual topology.

[1] Ferey, G., Chemical Society Reviews 37 (2008) 191.
[2] Czaja, A. U., Trukhan, N. and Muller, U., Chem. Soc. Rev. 38 (2009) 1284.
[3] Alaerts, L., Seguin, E., Poelman, H., Thibault-Starzyk, F., Jacobs, P. A. and De Vos, D. E. Chem.-Eur. J. 12 (2006) 7353.

E-mail: Matthias.Vandichel@Ugent.be www: http://molmod.ugent.be/