

Modeling aldol condensations in UiO-66 type materials

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Hybrid framework compounds including both inorganic and organic moieties have recently developed into an important new class of crystalline porous materials, also known as metal organic frameworks (MOFs) [1]. MOFs contain many metal sites, which might be catalytically active. This implies that MOFs have the potential to replace homogenous catalysts in important industrial applications [2]. Notwithstanding the catalytic activity of some of them- it is not always clear what the active sites are and how the reactions are catalyzed. In this contribution, we will focus on certain variations of the UiO-66. Recently, the UiO-66-NH₂ has successfully been applied experimentally for the synthesis of Jasminaldehyde from benzaldehyde and heptanal [3]. The presence of the coordinatively unsaturated Lewis acid sites in the material could be increased using a monocarboxylate modulation approach and post synthetic heat treatment [4]. To fully understand the mechanism of Jasminaldehyde condensation on such open active Zr-sites, we applied molecular modeling techniques on extended cluster as well as on periodic models of the UiO-66-X materials. On an extended cluster, the most plausible condensation reaction mechanism was found, showing that benzaldehyde and heptanal are adsorbed and activated on adjacent Zr sites before the coupling reaction. On the UiO-66-NH₂ model, there should be also an alternative reaction route, where one of the two aldehydes is activated on the amino group, explaining the higher selectivity of the UiO-66-NH₂ compared to the UiO-66 [3]. Deeper insight into these complex mechanisms allows us to explain the selectivity and activity on the UiO-66 type materials.

- [1] Férey, G., *Chemical Society Reviews* 37 (2008) 191.
- [2] Czaja, A. U., Trukhan, N. and Muller, U., *Chem. Soc. Rev.* 38 (2009) 1284.
- [3] Vermoortele, F., Ameloot, R., Vimont, A., Serre, C., De Vos, D., *Chemical Communications* 47 (2011) 1521.
- [4] Vermoortele, F., Bueken, B. Le Bars, G., Van de Voorde, B., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., Van Speybroeck, V., Kirschhock, C., De Vos, D., *Journal of the American Chemical Society* 135 (2013) 11465.