# 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-$NH_2$ 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-$NH_2$ 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-$NH_2$ 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.

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