Title: Modelling the effect of linker substituents on reactions in MOFs

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Abstract: Nowadays, Metal-organic frameworks (MOFs) attract increasing interest in catalysis. In this talk, we will discuss the construction of accurate catalyst models to describe various reaction classes within those heterogeneous nanoporous materials and compare them with equivalent homogeneous catalysts for their activity (1-5).

In the first part, two MOFs containing Lewis acid sites (UiO-66 and Cu_{3}BTC_{2}) will be compared with the industrially used homogeneous catalysts (ZrBr_{2} and ATPH) for the citronellal cyclization (1-2). In the second part, we will focus on the epoxidation of cyclohexene with tert-butylhydroperoxide (TBHP) and compare the heterogeneous catalyst MIL-47 with the homogeneous VO(acac)_{2} (3-5).

Experimentally, linear free energy relationships have been found when the reactions were performed on linker substituted variants of the V- and Zr-MOFs, showing that the electronic effects of linker substitution (-X) can be used as a tool to modulate the activity of the material. The relative conversion \( k_{X}/k_{H} \) in function of a substituent constant \( \sigma \) does then obey a Hammett equation. If the actual nature of the active site within the MOF is identified, a substituted cluster model can easily be constructed to reproduce these trends with first-principles chemical kinetics (2,5).

References
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