Title:

Modelling the effect of linker substituents on reactions in MOFs

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Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will ‘expand’ over 2 pages as you add text/diagrams into it.)

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_3BTC_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 σ 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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