

Design of enantioselective catalysts in MOF architectures: a combined computational and experimental approach

Thomas Bogaerts^{*,1,2}, Andy Van Yperen-De Deyne², Matthias Vandichel², Ying-Ya Liu¹, Veronique Van Speybroeck², Pascal Van Der Voort¹.

1 – Center for Ordered Materials, Organometallics and Catalysis, krijgslaan 281 Ghent University, 9000 Ghent, Belgium

2 – Center for Molecular Modeling, Technologiepark 903 Ghent university, 9052 Zwijnaarde, Belgium

* corresponding author: thomas.bogaerts@ugent.be

In the last decades salen complexes have proven their value as chiral epoxidation catalysts [1]. The original manganese-salen complex allows the enantioselective epoxidation of unfunctionalized olefins with an enantiomeric excess of over 90% [2]. To improve the applicability of this catalyst, a route towards the development of a heterogeneous catalyst is proposed where the complex is trapped inside the cages of a nanoporous material. This material should have sufficiently big internal cages to host the complex. A metal-organic framework, MIL101(Al)[3] is chosen as carrier; this structure is similar to the framework first published by Ferey *et al.*[4] This system has internal cavities of over 30Å, which are large enough to contain the complex. Catalytic tests have shown that the heterogeneous catalyst has the same selectivity as the homogeneous complex, while the carrier improves the reusability and stability. The obtained catalyst was thoroughly characterized using various spectroscopic techniques such as IR, XRF, ...

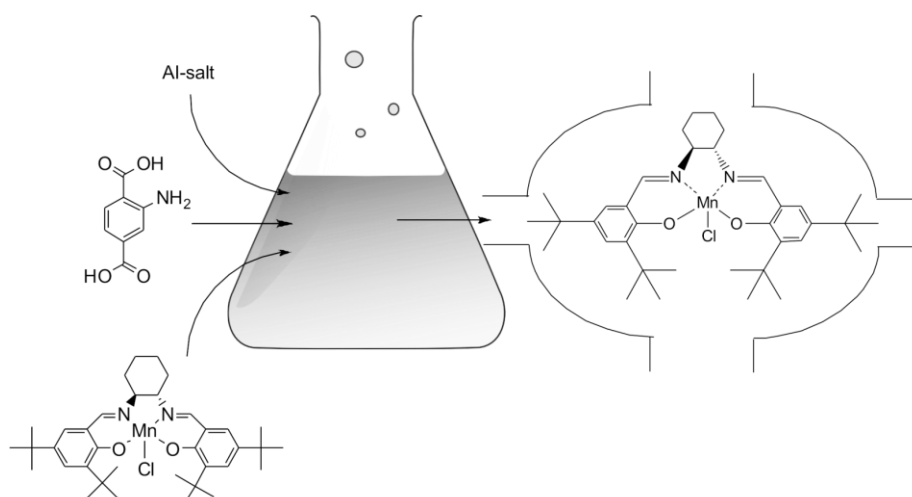


Figure 1: Principle of the encapsulation, by using a one-pot synthesis the salen complex is encapsulated in the pores of the framework.

To fully understand the mechanism of epoxidation by the salen complex, molecular modeling was used. The salen complex at hand has been proven challenging to model accurately. To select a reliable computational protocol, a benchmark study was performed to select the most appropriate DFT functional, by comparing them to CASSCF calculations performed by Sherrill *et al.*[5] The OPBE functional was found to give accurate results. This allows us to elucidate the most probable reaction mechanism and give an insight in the reasons for the enantioselectivity of the salen catalyst. The first results show that the favored mechanism is dependent on the spin state, with a two-step mechanism being favored. The combined experimental and theoretical approach allows designing of a heterogeneous catalyst that offers similar selectivity as the homogeneous salen-complex in the enantioselective epoxidation of unfunctionalized olefins. Further catalytic and selectivity tests are in progress to validate this concept.

- [1] Katsuki, T., *Coord. Chem. Rev.*, (1995) **140**, 189.
- [2] Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L., *J. Am. Chem. Soc.*, (1991) **113**, 7063.
- [3] Hartmann, M.; Fischer, M., *Microporous Mesoporous Mat.*, (2012) **164**, 38.
- [4] Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I., *Science*, (2005) **309**, 2040.
- [5] Sears, J. S.; Sherrill, C. D., *J. Chem. Phys.*, (2006) **124**, 144314.