Immobilization of a chiral salen catalyst, a grafting versus an encapsulation approach

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Introduction

For the production of bulk chemicals zeolites and other porous heterogeneous catalysts have found their place as the dominant technology. However in the fine chemical industry many well-known processes are catalysed by homogeneous catalysts where no immediate heterogeneous analogue is available. A good approach to design a heterogeneous catalyst for these processes is the immobilization of the known homogenous catalyst on a solid support.[1] Here we present this approach applied on a Jacobsen type complex. These complexes are known for their applicability in the epoxidation of unfunctionalized olefins obtaining over 90% enantiomeric excess.[2] To further increase the potential use of this catalyst we propose two different immobilization procedures and analyse the results by means of ab initio molecular modelling.

Results and Discussion

In a first procedure, the salen complex is covalently grafted in the pores of a MIL101(Cr) metal organic framework (MOF).[3] This hybrid material was chosen for its large pore size that can contain the active complex and its high stability. A catalytic test shows a decreased conversion and selectivity after the grafting procedure. This can be explained by the molecular modelling study, which shows the use of asymmetric complexes, that are needed for the grafting, induces a decrease in enantioselectivity. However, the open structure of the MOF makes it a very suitable host since the decrease in selectivity is limited compared to previous studies where grafting was applied.[4]

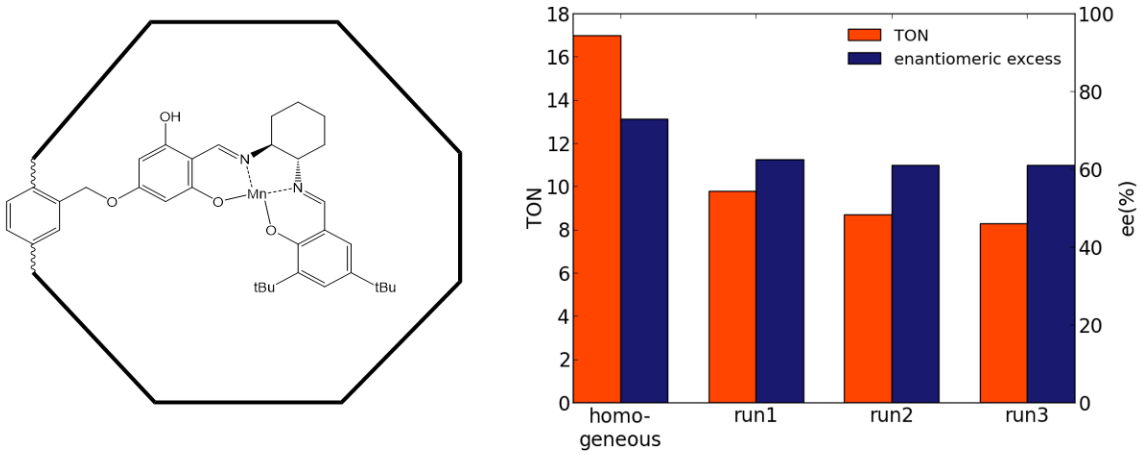

Figure 1. The grafting approach and its catalytic results

The second approach aims to omit the dependence on asymmetric variants of the Jacobsen complex. The *tert*-butyl groups, that are not present on one side of the asymmetric complex used in the grafting procedure, were shown to be critical for obtaining a high selectivity. Therefor a detailed analysis of the space required for the complex and the important transition

state was obtained from the modelling study, which shows the pores of a MIL101-type MOF are large enough to accommodate this system without limitations. Therefor a procedure was developed where the metal organic framework was grown around the complex, forming a 'ship-in-a-bottle' catalyst.[5] This catalyst showed no decrease in selectivity which indicates there is no interference from the carrier material, as was the case with the first approach.

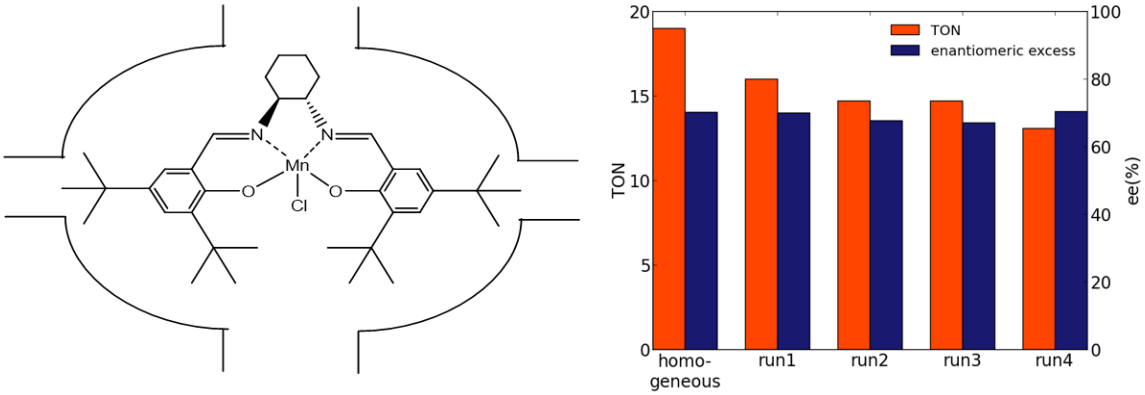

Figure 2. The ship-in-a-bottle approach and associated catalytic results

Conclusions

From these results we can conclude that when immobilizing an existing homogeneous catalyst on a solid support care should be taken to choose a procedure that limits the influence on behaviour of the complex. For the Jacobsen complex this can be obtained by encapsulating it in a metal organic framework. The results are supported by a molecular modelling study that shows the critical factors in the structure of the catalyst and provides more insight in the mechanism of the selectivity.

Acknowledgements

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