Effect of linker substituents on the epoxidation performance of V-MIL-47

Matthias Vandichel[1], Karen Leus[2], Yingya Liu[2], Michel Waroquier[1], Pascal Van Der Voort[2] and Veronique Van Speybroeck[1]

[1] *Center for Molecular Modeling, Ghent University, Belgium*
[2] *Center for Ordered Materials, Organometallics and Catalysis, Department of Inorganic and Physical Chemistry, Ghent University, Belgium*
*Matthias.Vandichel@Ugent.be*

Introduction

Metal Organic Frameworks (MOFs) are crystalline porous solids composed of a three-dimensional network of metal ions held in place by multidentate organic molecules. In recent years, MOFs have received considerable attention as potentially valuable materials for gas storage and catalysis. Until now, most of the studies on the catalytic activity of MOFs are focused on structures that contain coordinative unsaturated metal sites, as it is often believed that the coordinative saturated MOFs will not be catalytically active. In this contribution we will discuss the catalytic performance of a completely saturated Metal Organic Framework, V-MIL-47 [1], for the oxidation of cyclohexene [2]. In this case, the catalytic activity need to be explained by accessible surface sites or internal defects. Furthermore, the influence of the amine and nitro functionalized MIL-47 on the oxidation of cyclohexene will be discussed theoretically and experimentally. These new MIL-47 analogues with extra electron donating or withdrawing groups will be compared to the conventional MIL-47 for the oxidation of cyclohexene. Moreover a catalytic cycle, based on molecular modeling on the non-substituted V-MIL-47 will be presented. Also, the effect of substituents on radical generation regeneration of the catalyst will be discussed.

Theoretical section

Geometry optimizations were first performed with the Gaussian03 package using the B3LYP hybrid functional. The double-zeta Pople basis set 6–31+G(d) was used for all the atoms except vanadium, for which the LANL2DZ effective core potential was applied. Even though this methodology was used for the calculation of the frequencies and the construction of Table 1, the energies will be refined by single point energy calculations at the b3lyp/6-311+g(3df,2p)-D3 level of theory. The fastest activated epoxidation mechanism via vanadium *tert*-butylperoxo complexes was taken from earlier results [2,3] and happens via a $V^{+IV}O(OOtBu)$ complex. To account for the substituent effect in this complex, the two linkers in the cluster model of MIL-47 (Figure 1) were modified. For clarity, only one out of four relevant orientations of the linker substituents is shown in Figure 1.

The calculation of kinetic parameters is done by an in-house developed software module TAMkin [4]. As the pre- and post-reactive complexes, immediately formed from the transition state are not discussed, only apparent energy differences will be discussed (no intrinsic barriers).
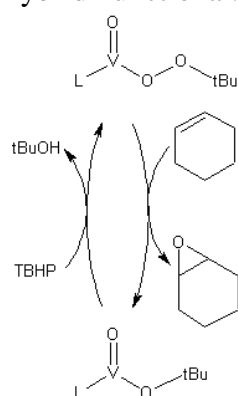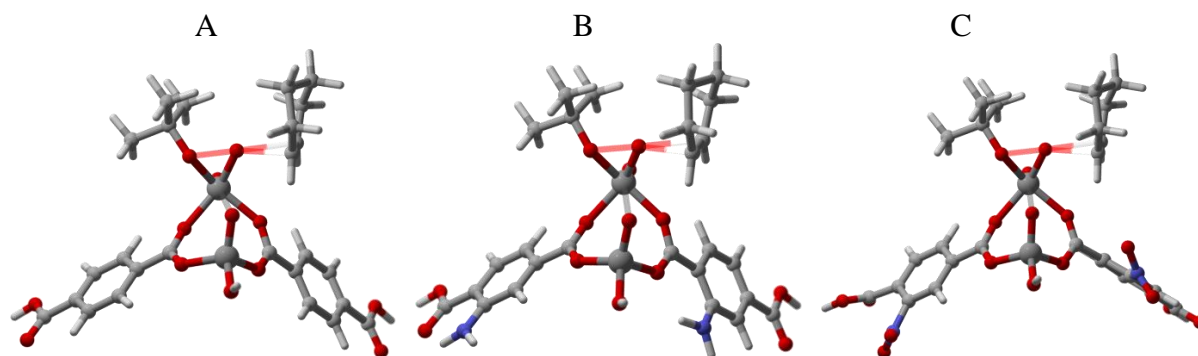
Figure 1: Examples of epoxidation transition states on a MIL-47 clusters with two terephtalic linkers: (A) normal MIL-47, (B) MIL-47(NH$_2$); (C) MIL-47(NO$_2$)

Results and discussion

Table 1 gives us an overview of the bimolecular kinetic parameters fitted between 273 and 373 K for model systems A, B and C (Figure 1). Those three systems can be ordered on the basis of the epoxidation rate: C > A > B.

Table 1. The pre-exponential factor (A$_{fwd}$, 1/s), the activation energy (E$_{a,fwd}$, kJ/mol), the kinetic rate coefficient at 323 K (k$_{fwd}$, mol m^{-3} s^{-1}) and the free energy barrier for the transition state at 323 K (ΔG$_{323}$, kJ/mol) are shown for the epoxidation reaction.

Cluster model	A$_{fwd}$ (1/s)	E$_{a,fwd}$ (kJ/mol)	k$_{fwd}$ (323K) (mol m^{-3} s^{-1})	ΔG$_{323}$ (kJ/mol)
A	3.71E+04	61.9	3.58E-06	103.3
B	3.81E+03	61.0	5.11E-07	108.5
C	2.28E+04	57.1	1.29E-05	99.8

Conclusions

Various linker modifications of V-MIL-47 have been tested experminentally and theoretically for the epoxidation of cyclohexene with TBHP. In this contribution, theoretical calculations confirm how various linker substituents affect the epoxidation behavior. In summary, the epoxidation reaction accelerates with electron withdrawing substituents, while it decelerates with electron donating substituents.

Acknowledgements

References

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