XRF analysis

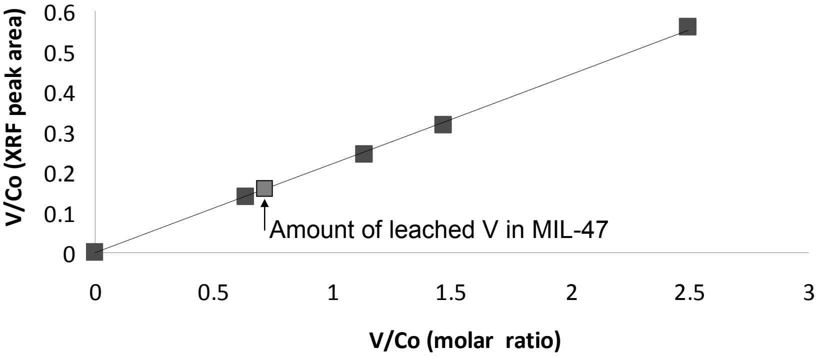

Figure S.1 Calibration curve: V/Co peak area as a function of the V/Co molar ratio

XRF measurements were performed on a Bruker combined XRD/XRF home made facility. The measurements were performed by adding known amounts of a Co-salt to the solution. Spectra were accumulated for 100 s.

Nitrogen adsorption

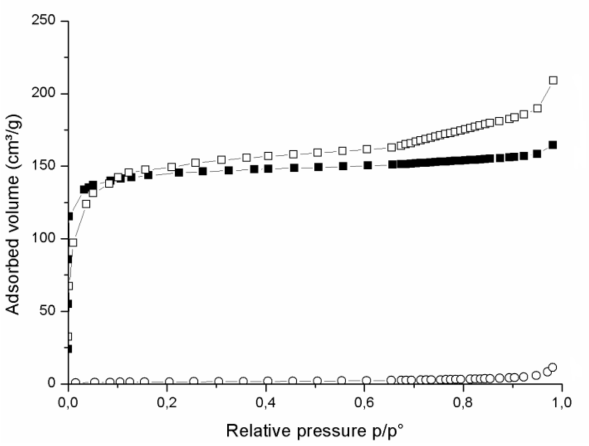

Figure S.2 Nitrogen adsorption isotherms of MIL-47 (■) before, (○) after the first catalytic run and (□) after regeneration.

XRD patterns

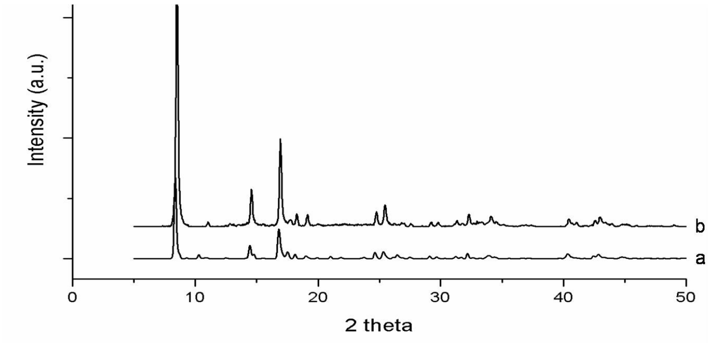

Figure S.3 XRD patterns of MIL-47 (a) before and (b) after regeneration.

Cyclohexene conversion curves of the VO_x/SiO_2 catalyst

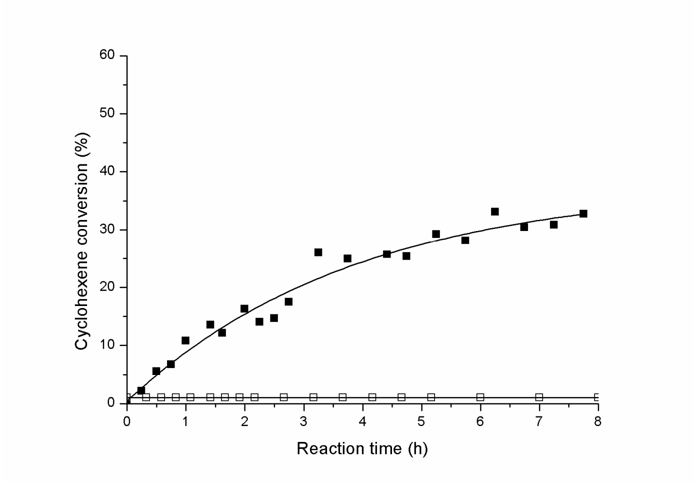

Figure S.4 Cyclohexene conversion curves of the VO_x/SiO_2 catalyst in its first (closed squares) and second run (open squares). VO_x/SiO_2 catalyst synthesis: 1g porous silica (silicagel 60) was dried at 400°C and subsequently stirred in 30 ml 0.02M NH_4VO_3 solution at 80°C for 2 hours. The as-made catalyst was filtrated and dried, followed by a calcination step in air at 550°C (heating rate: 1.5°C/min). The cyclohexene oxidation was carried out in a 2 neck flask with 0.1g catalyst (loading: 0.2 mmol V/g) in chloroform using TBHP in water as oxidans at 50°C. 1,2,4-trichlorobenzene was used as an internal standard. The molar ratios were chloroform:cyclohexene:TBHP:1,2,4-trichorobenzene = 462:1:2:1.

Geometrical comparison of MIL-47 and $VO(acac)_2$

To describe the surroundings of the vanadium atom in the most faithful way, we concentrated in first instance the epoxidation on $VO(acac)_2$, which has similar surroundings as the Vanadium in MIL47. This resemblance is clearly indicated in Figure S.5 (also present in the article text) and S.6, where MIL-47 (as obtained experimentally from XRD-data) is compared with $VO(acac)_2$ (optimized as indicated in the computational methods section).

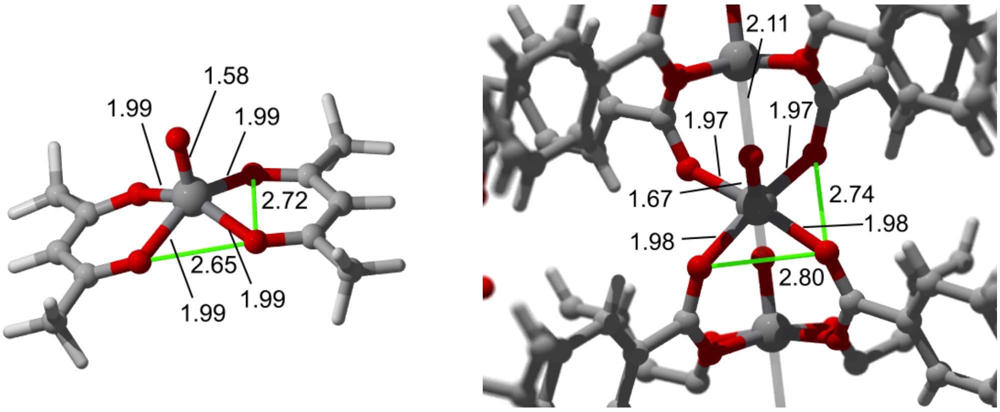

Figure S.5 Comparison of distances (given in Å) for $VO(acac)_2$ and MIL-47.

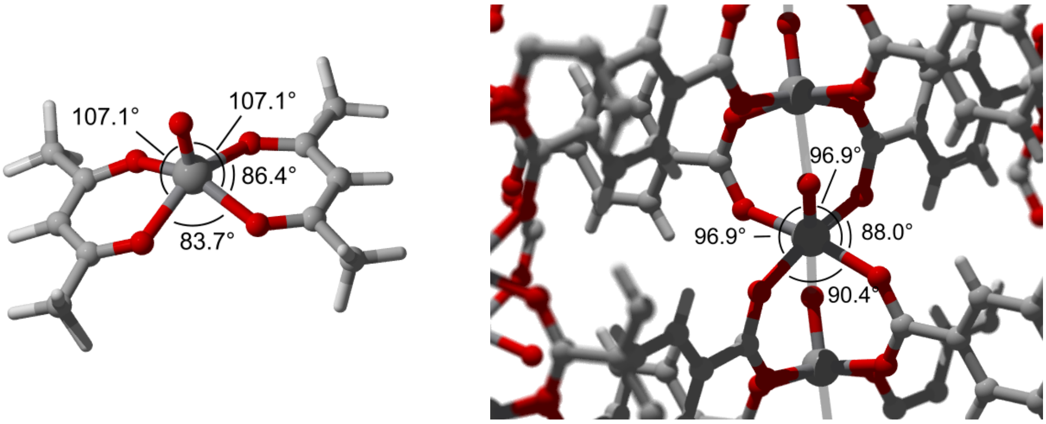

Figure S.6 Comparison of angles (given in °) for VO(acac)$_2$ and MIL-47.

Computational methods

The catalytic cycle for the homogeneous epoxidation of cyclohexene [VO(acac)$_2$ + TBHP] was obtained by complete optimization in vacuum of all intermediates. Geometry optimizations were first performed with the Gaussian03 package [1] using the B3LYP hybrid functional [2-3]. 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 [4]. Even though this methodology was used for the calculation of the frequencies, the energies were refined by single point energy calculations with the b3lyp/6-311+g(3df,2p) level of theory. The results for different functionals are shown in Table S.1.
This type of procedure is commonly used in theoretical calculation concerning transition metal catalysis [5-7]. An overview of the optimized molecules is given in Figure S.6.

It is important to note that our cycle contains two types of reactions: A and P were modeled as equilibrium steps between two reactants (r1, r2) and two product (p1, p2). Furthermore, for the reactions E and R transition states where calculated. For each transition state (TS), an IRC calculation was carried as starting point to find the correct pre-TS reactants and post-TS products. Rate coefficients k (1/s) were obtained in a unimolecular way by using transition-state theory (TST) by calculating the partition functions (q_R, q_{TS}, q_P) at T (323 K):

$$k_{forward} = k_{fwd} = \frac{q_{TS}}{q_R}\exp\left(-\frac{\Delta E_{0,fwd}}{R.T}\right)$$
$$k_{backward} = k_{bwd} = \frac{q_{TS}}{q_P}\exp\left(-\frac{\Delta E_{0,bwd}}{R.T}\right)$$

The unimolecular approach makes also use from the fact that reactants, transition states and products are solvated in a approximately the same way in the reaction mechanism. Figures from those stationary points are indicated in figures S.7 and S.8.

The calculation procedures for k and K are now implemented in an in-house developed software module TAMKIN, which will be released shortly [8].

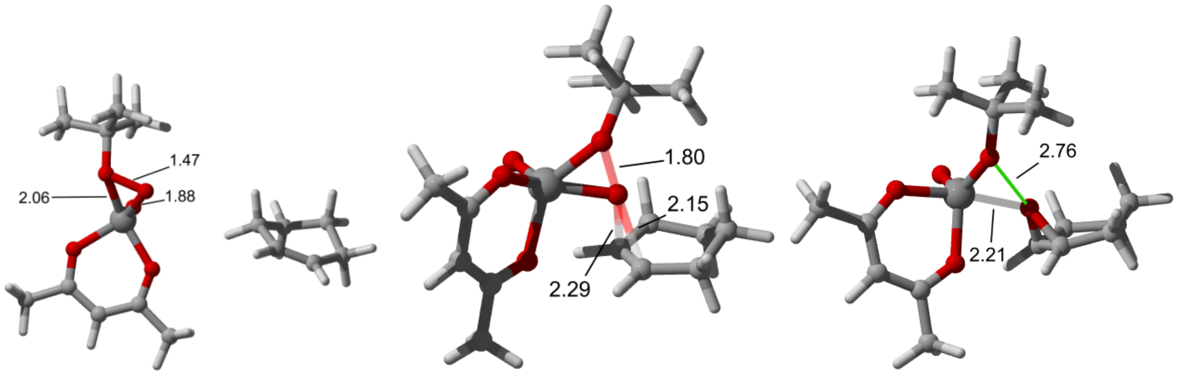

Figure S.7: The reactant, transition state and product for the epoxidation reaction (E) between VO(acac)(OOtBu) and cyclohexene.

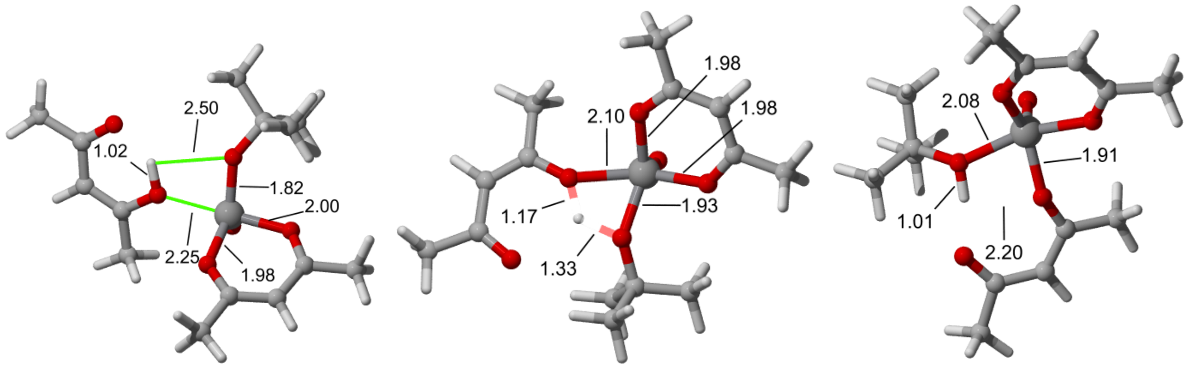

Figure S.8: The reactant, transition state and product for the regeneration reaction (R) of VO(acac)(OtBu)(Hacac).

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