

# The catalytic performance of MIL-47 in the liquid phase oxidation of cyclohexene

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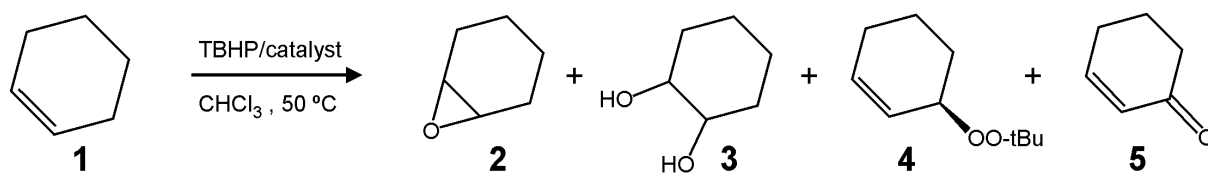
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## Introduction

Metal Organic Frameworks (MOFs) are crystalline organic-inorganic porous solids that build up a three-dimensional framework. This relative new family of porous materials possesses some very attractive features: a high micropore volume, crystallinity and a significant metal content offering potentially valuable active sites. Recently, the catalytic applications of MOFs have been reviewed by Hupp et al. and Farrusseng et al. [1,2]. However, catalytic reaction mechanisms in Metal Organic Frameworks and in particular at saturated coordinated centres are still poorly understood.

In the present work, we have tested MIL-47 for its catalytic performance in the oxidation of cyclohexene and compared with the catalytic activity of the homogeneous catalyst VO(acac)<sub>2</sub> [3]. The selective oxidation of cyclohexene is particularly interesting as it can yield, depending on the catalyst and the reaction conditions, several products as shown in scheme 1. Amongst the various oxidation products of cyclohexene, cyclohexane epoxide is a highly reactive and selective organic intermediate which is widely used in the synthesis of enantioselective drugs, epoxy paints and rubber promoters [4].



Scheme 1

Furthermore the heterogeneity, stability and regeneration capacity of the V-containing MOF were examined.

## Experimental section

The hydrothermal synthesis of MIL-47 is based on a literature procedure [5]. A mixture of  $VCl_3$ , terephthalic acid and  $H_2O$  (molar ratio 1/0.25/100) is brought into a Teflon lined steel autoclave, which is heated at 473 K for 4 days. A calcination step is performed at 573 K to remove the excess of terephthalic acid in the pores.

After a catalytic run, MIL-47 is regenerated by a treatment in a tubular furnace under a  $N_2$ -flow at 523 K, to remove the organic compounds in the pores.

## Results and Discussion

The oxidation of cyclohexene was carried out in a three neck flask under an inert atmosphere using *tert*-butyl hydroperoxide in water as oxidant, 1,2,4-trichlorobenzene as internal standard and chloroform as solvent. The molar ratio cyclohexene:oxidant is 1:2. The reaction mixture was stirred at 50° C. Samples were taken out from the reaction mixture at certain times and were analyzed with a Trace GC Ultra (Finnigan), fitted with an capillary column (10m, 0,1 mm, 0,4  $\mu$ m) and an FID detector. Blanc reactions were performed without catalyst. No cyclohexene conversion is observed without catalyst. Figure 1 depicts the cyclohexene conversion for MIL-47 and the homogeneous  $VO(acac)_2$  catalyst (using the same amount of V sites).

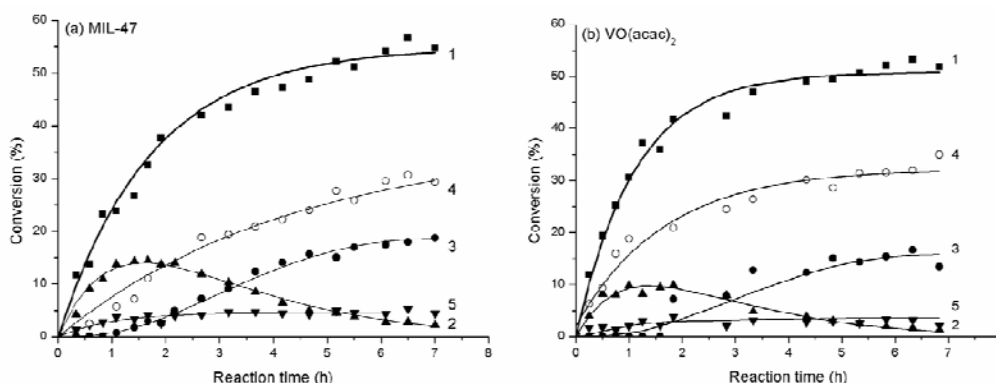


Figure 1 Total cyclohexene conversion and detailed product distribution with (a) MIL-47 and (b)  $VO(acac)_2$ .

From this figure, it can be seen that there is a good similarity between the 2 catalysts. Both catalysts show high reaction rates for the conversion of cyclohexene and a similar product distribution [3]. The initial turn over frequencies are  $57\text{ h}^{-1}$  and  $43\text{ h}^{-1}$  for the  $VO(acac)_2$  and the MIL-47 respectively (after 20 minutes of reaction) whereas

the turn over numbers calculated at the end of the reaction were 62 and 68 for the  $\text{VO}(\text{acac})_2$  and the MIL-47 respectively.

To examine the heterogeneity of the catalytic reaction, a hot filtration experiment was performed after 1h of reaction using a combined nylon-membrane filter. Figure 2 presents the conversion curve of cyclohexene in the presence of MIL-47 and the cyclohexene conversion after filtration. Also the sum of products 2, 3 and 5 is shown with and without the hot filtration.

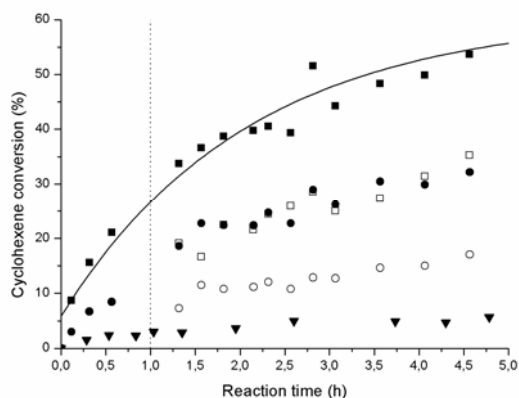


Figure 2. Hot filtration experiment. Cyclohexene conversion (■) and yield of oxidized products (●) as a function of time. Cyclohexene conversion (□) and yield of oxidized products (○) after filtration of the catalyst. The catalytic activity of  $\text{VO}(\text{acac})_2$  corresponding to the 12,8% leached V-sites (▼).

It is clear from this figure that both the conversion of cyclohexene and the formation of oxidized products is strongly reduced after filtration of the catalyst. This indicates that the catalytic reaction is predominantly heterogeneous. There is however some homogeneous catalytic activity left. This activity is due to a combination of radical mechanisms (formation of product 4 occurs via radical pathways) and leached V. By XRF analysis we have determined that 12,8% of the V-sites has leached out after 1 h of reaction. Finally, we also show the catalytic conversion caused by dissolving exactly the amount of  $\text{VO}(\text{acac})_2$  that corresponds to the 12,8% leached V-sites (▼). This leads however to only 5% conversion.

The stability of MIL-47 after a first catalytic run was verified by nitrogen adsorption measurements and X-ray diffraction measurements (see figure 3). From this figure it can be clearly seen that the MIL-47 shows no loss of surface area after a first run and that the crystalline structure of the MIL-47 is preserved after regeneration.

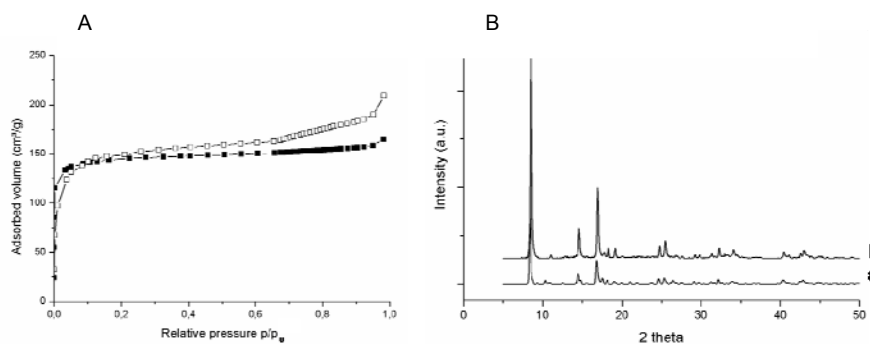


Figure 3. A) nitrogen adsorption isotherm of MIL-47 before (■) and after (□) regeneration B) XRD patterns of MIL-47 before (a) and after regeneration (b).

To evaluate the regeneration capacity of this novel catalyst, MIL-47 was tested for a second catalytic run. In figure 4 the second run experiment is shown using 27 mg of MIL-47. To make a fair comparison the first run experiments using 20 mg and 40 mg of MIL-47 are also presented in figure 4. This figure shows that no loss in activity of MIL-47 is observed during this second run experiment.

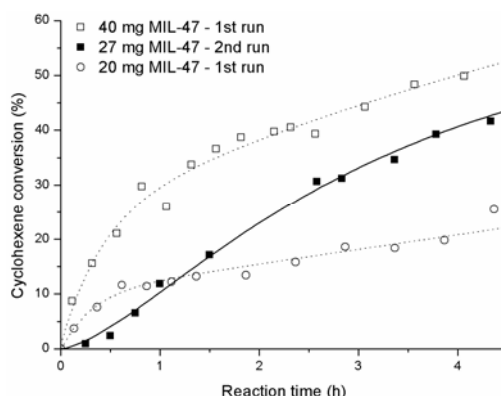


Figure 4 Cyclohexene conversion for MIL-47 in ist first run with (□) 40 mg MIL-47, (○) 20 mg MIL-47 MIL-47 catalyst mass and (■) after regeneration with 27 mg MIL-47.

In conclusion, MIL-47 is catalytically active in the oxidation of cyclohexene. Hot filtration experiments have proved that the catalysis is predominantly heterogeneous. Furthermore MIL-47 can be regenerated and reused.

## References

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