

A coordinative saturated vanadium containing Metal Organic Framework that shows a remarkable catalytic activity

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Abstract

A completely saturated Metal Organic Framework, MIL-47 was synthesized and tested for its catalytic performance in the oxidation of cyclohexene with *tert*-butyl hydroperoxide as oxidant. The catalyst was compared to several reference catalysts: namely VAPO-5, supported VO_x/SiO₂ and the homogeneous catalyst VO(acac)₂. MIL-47 shows a remarkable catalytic activity and preserves its crystalline structure and surface area after a catalytic run. Furthermore MIL-47 exhibits a very high activity in successive runs.

Keywords: Metal Organic Frameworks, vanadium, oxidation, liquid phase

1. Introduction

Metal Organic Frameworks (MOFs) are crystalline porous solids composed of a three-dimensional (3D) network of metal ions held in place by multidentate organic molecules [1,2]. In recent years, MOFs have received considerable attention as potentially valuable gas storage and catalyst materials [3-7]. MOFs possess several attractive features: a high micropore volume, crystallinity and a high metal content offering potentially valuable active sites.

So far, only a few catalytic applications of Metal Organic Frameworks have been reported. Some of their potential applications were outlined recently in two excellent reviews [8,9]. All these reports deal with Metal Organic Frameworks that have unsaturated sites. However, to obtain insight into the real nature of the active sites, it is of a paramount importance to study saturated Metal Organic Frameworks.

Therefore, a completely saturated, vanadium containing MOF was synthesized, namely MIL-47. This MOF is a porous terephthalate built from infinite chains of V⁴⁺O₆ octahedra, held together by dicarboxylate groups of the terephthalate linkers and has a three-dimensional orthorhombic structure [10].

In the present work, we have tested MIL-47 for its catalytic performance in the oxidation of cyclohexene. 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 [11]. Furthermore the catalytic activity of MIL-47 is compared to VAPO-5, VO_x/SiO_2 and the homogeneous catalyst $\text{VO}(\text{acac})_2$.

2. Experimental section

The hydrothermal synthesis of MIL-47 is based on a literature procedure [10]. 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. In a next step, MIL-47as is brought at 573 K for 22 h and 30 min to remove the excess of terephthalic acid in the pores. VAPO-5 is synthesized as described previously: a solution of oxovanadium (IV) sulphate-hydrate and a solution of H_3PO_4 are mixed together. While stirring, pseudo boehmite (from Sasol) and triethylamine are added. In a further step, the gel is brought into an autoclave and placed in an oven at 443 K for 2 days. By centrifugation, the solid is recovered. Furthermore the catalyst is dried and calcinated under a O_2 -flow [12]. For the synthesis of VO_x/SiO_2 , Kieselgel 60 is stirred in a NH_4VO_3 -solution at 338 K for 2 h. Afterwards, the solid is filtered and dried during 2 h at 373 K, followed by a calcination at 823 K during 5 h.

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

3. Results and discussion

The oxidation of cyclohexene was carried out in a three neck flask under an inert atmosphere. To a solution of cyclohexene (0.05 mol), *tert*-butyl hydroperoxide (0,14 mol) and 1,2,4-trichlorobenzene (0.05 mol) (used as internal standard) in chloroform (0.38 mol) 0,1 g of the catalyst was added. The reaction mixture was stirred at 50° C. All the samples were analyzed with a Trace GC Ultra (Finnigan), fitted with an capillary column (10m, 0,1 mm, 0,4 μm) and an FID detector. Blanc reactions were performed without catalyst.

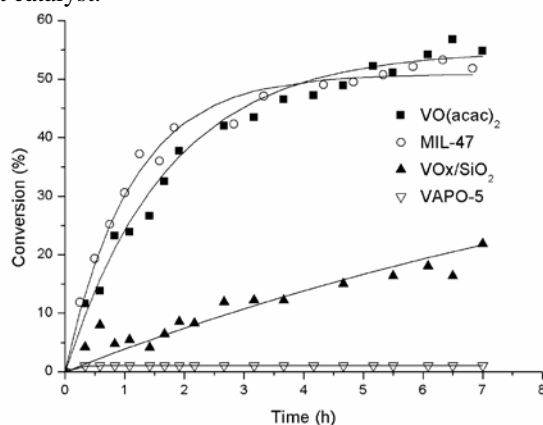


Fig. 1 Conversion curve of cyclohexene for (■) unsupported $\text{VO}(\text{acac})_2$, (○) MIL-47, (▲) VO_x/SiO_2 and (▼) VAPO-5.

In Figure 1, the conversion curve of cyclohexene is presented in comparison with the three reference catalysts. As can be seen in Figure 1, VAPO-5 is catalytic inactive for the oxidation of cyclohexene, whereas the three other catalysts: MIL-47, the supported VO_x/SiO_2 and the homogeneous $\text{VO}(\text{acac})_2$ exhibit a very high catalytic activity.

The turn over number (TON) of MIL-47 is calculated, based on the amount of cyclohexene that is converted. The TON of MIL-47 was approximately 108 after eight hours of reaction. Thermal Gravimetric Analysis experiments (TGA) were performed on MIL-47 before and after a catalytic run to quantify the amount of leached vanadium. In comparison with the supported vanadium oxide catalyst, only a small amount of vanadium is leached. The leaching was less than 20% in the first run with MIL-47, whereas the VO_x/SiO_2 showed a leaching of more than 40%. Furthermore, the catalyst was recovered after a first catalytic run. The X-ray diffraction patterns of MIL-47 before and after regeneration are shown in Figure 2.

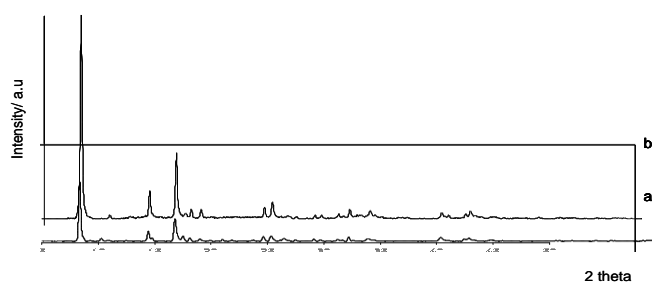


Fig. 2 XRD patterns of MIL-47 (a) before and (b) after regeneration.

MIL-47 preserves its crystalline structure after regeneration, as can be seen from Figure 2. Moreover, the nitrogen adsorption experiments of MIL-47 before and after regeneration are presented in Figure 3. Note that the MIL-47 shows no loss at all of surface area and pore volume after regeneration.

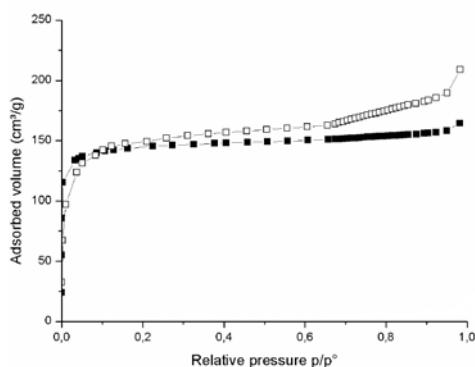


Fig. 3 Nitrogen adsorption isotherms of MIL-47 (■) before and (□) after regeneration.

To evaluate the regeneration capacity of this novel catalyst, MIL-47 was tested for a second catalytic run and compared to the vanadium oxide catalyst. The conversion of cyclohexene for MIL-47 and the VO_x/SiO_2 catalyst in the first and second run is shown in Figure 4.

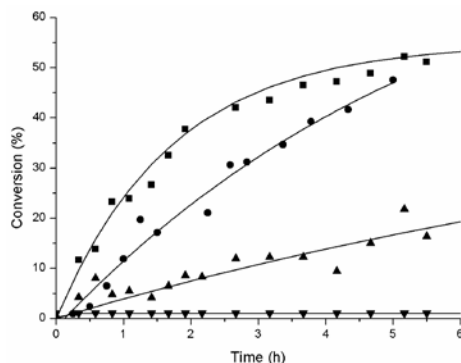


Fig. 4 Conversion of cyclohexene for MIL-47 in its (■) first run, (●) second run and VO_x/SiO₂ (▲) first and (▼) second run.

MIL-47 still shows a high conversion of cyclohexene, whereas the supported VO_x/SiO₂ shows no activity at all in its second run due to leaching of the vanadium centers. This observation indicates that MIL-47 acts as a truly heterogeneous catalyst.

In conclusion, the saturated Metal Organic Framework, MIL-47, is investigated for its catalytic activity for the oxidation of cyclohexene and compared to three reference catalysts. MIL-47, containing saturated vanadium centres, shows a high catalytic conversion. X-ray diffraction measurements and nitrogen adsorption experiments prove the stability of this new catalyst under oxidation reactions. Furthermore MIL-47 exhibits a very high catalytic activity in successive runs.

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