A study of the effect of electron donating and electron withdrawing groups on the catalytic performance of V-MIL-47

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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 discuss the catalytic performance of a completely saturated Metal Organic Framework, V-MIL-47 [1], in the oxidation of cyclohexene [2]. This MOF was compared with several vanadium containing reference catalysts: $VO(acac)_2$, VAPO-5 and VO_x/SiO_2, showing that MIL-47 exhibits a high catalytic performance and an interesting product distribution as can be seen in the figure below.

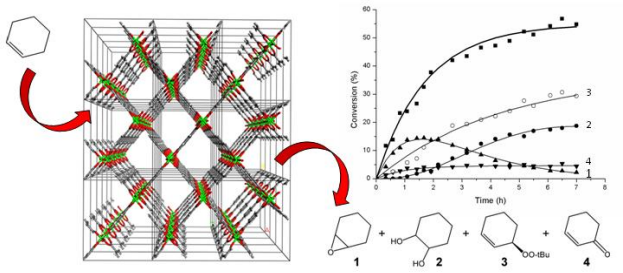

Figure: The catalytic performance of MIL-47

Subsequently, we have synthesized the amine and nitro functionalised MIL-47. The latter was synthesized by an oxidation of the amine group [3]. The catalytic performance of these MIL-47 analogues with extra electron donating or withdrawing groups will be discussed in comparison to the conventional MIL-47 in the oxidation of cyclohexene. All systems have also been modelled on the B3LYP/6-311+g(3df,2p) level of theory to calculate the reaction kinetics.

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[3] Rajender Reddy K., Uma Maheswari C., Venkateshwar M., Lakshmi Kantam M., Advanced Synthesis and Catalysis 351 (2009) 93.

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