Synthesis of new Vanadium containing Metal Organic Frameworks (V-MOFs) for applications in oxidation catalysis and adsorption/separation processes

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Metal Organic Frameworks (MOFs) can be considered as the most recent development in the field of ordered porous materials. MOFs are crystalline atomically ordered materials, with an almost unlimited choice of building bricks, allowing a very precise control over morphology, pore size and functionalities in the walls. This new class of hybrid materials has already been extensively studied for gas storage[1], separations[2] and luminescence properties[3]. Also they become more and more a topic of interest in heterogeneous catalysis[4]. The heterogenization of existing catalysts is of a paramount importance to achieve the goal "sustainable and green chemistry". Because of their outstanding characteristics (high pore volume and surface area) MOFs are often seen as the new generation of "superzeolites". Almost every transition metal ion and many different organic linkers can be used to obtain an MOF structure, what makes the plausible metal-ligand combinations endless. However, the reported V-MOFs are very rare. Nevertheless, these V-containing MOFs can show some great potential in oxidation catalysis. In collaboration with the CMM, we investigated the reported V-MOF, MIL-47, in the cyclohexene oxidation. MIL-47 has a three-dimensional framework, where each V^{+IV} center is coordinated to four oxygen atoms from four carboxylate groups, and to two oxygen atoms on the O–V–O axis, thus forming a saturated octahedral coordination node[5]. Lately, we published the first catalytic evaluation of V-MIL-47 in the liquid phase oxidation of cyclohexene, using *tert*-Butyl hydroperoxide (TBHP) in water as the oxidant[6]. In our more recent study, we utilized TBHP in decane as the oxidant in which the MIL-47 acted as a true heterogeneous catalyst[7]. Extensive computational modeling is performed to elucidate the reaction pathways, which are in agreement with the electron paramagnetic resonance (EPR) measurements (performed in collaboration with the Electron Magnetic Resonance (EMR) research group). Moreover, with theoretical modeling we were able to define the active catalytic sites and explain the role of the used solvent (water versus decane) on the product selectivity.

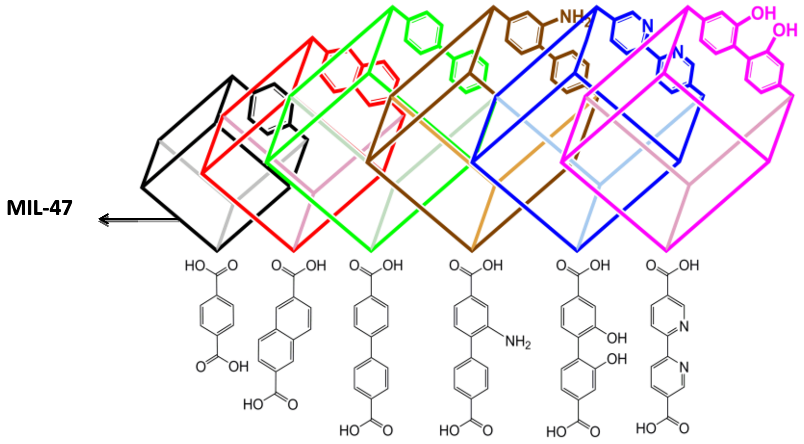

Fig. 1 Isoreticular series of MIL-47

Furthermore, our research group made a isoreticular series of the V-MIL-47 in which the organic linker is functionalized without changing the topology of the original MIL-47 structure (see Fig. 1). Thus, a series of functional groups (-NH$_2$, -OH, -CH$_3$, -Br) was grafted onto the organic linker, renders different applications[8]. Additionally, we synthesized new vanadium containing MOFs, denoted as COMOC-1, COMOC-2 and COMOC-3. The latter has been studied in our benchmark catalytic test and was compared with the conventional MIL-47[9], whereas the other two developed MOFs were examined for their adsorption properties in collaboration with the group of prof. Denayer at the VUB[10]. On all these new V-MOFs computational studies have been carried out to obtain insights in their adsorption properties, catalytic performance and even structural behavior. For COMOC-2 a free energetic breathing profile could be constructed by optimizing a chain of structures between the narrow and large pore form. Moreover, we reported for the first time a new theoretical procedure to model XRPD patterns of the intermediate structures. The resulted theoretical XRPD patterns corresponded nicely with the experimentally measured XRPD patterns[10].

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