

This thesis summarizes our efforts to contribute to the development of novel heterogeneous catalysts based on Metal-Organic Framework compounds (MOFs) with a remarkable high thermal and chemical resistance; namely MIL-101 and UiO-66 type compounds. Special emphasis has been placed in the simultaneous introduction of two different active sites, either accidentally or intentionally through linker functionalization or post-synthesis encapsulation. This strategy could lead to multifunctional catalysts that can act together synergistically in a dual activation mechanism or can catalyze two (or more) consecutive reactions in a cascade process. Accordingly, the results presented are organized into two blocks, depending on the number of reaction steps catalyzed by the MOF compound: One step reactions and Multistep reaction processes. Throughout this study, we have duly evaluated the true potential of the MOF with respect to other existing homogeneous and heterogeneous catalysts, and we have also assessed the stability and reusability of the material, which are two of the major objections raised when catalytic applications of MOFs are considered.

In the first block of results, the catalytic activity of various MOFs containing inorganic building blocks based on either  $Zn^{2+}$  (MOF-5 and IRMOF-3) or  $Zr^{4+}$  ions (UiO-66 type compounds) is evaluated for single step reactions. In particular, **Chapter 1** describes the use of  $Zn^{2+}$  MOFs as catalysts for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. The possible role of defects associated to either partial hydrolysis of the network or inclusion of ZnO particles during the MOF crystallization, have been considered to reevaluate previous existing reports and to explain the (somewhat unexpected) activity of MOF-5 for this reaction. To complete this block of results, we have assessed the performance of MOFs containing Zr oxoclusters as catalysts for the esterification of biomass derived carboxylic compounds: free fatty acids (**Chapter 2**) and levulinic acid (**Chapter 3**). Again, the role of lattice defects, associated to linker deficiencies, together with eventual dual activation mechanisms of the carboxylic compound and the alcohol, are considered to explain the observed trends in the catalytic activities of the compounds.

In **Chapter 4**, we describe the preparation of a bifunctional catalyst based on Pd nanoparticles encapsulated inside the mesoporous cages of MIL-101, and its use as catalyst for the one-pot conversion of citronellal into menthol. This transformation consists in a two step process in which the  $Cr^{3+}$  of the MOF first catalyze citronellal isomerization to isopulegol, followed by the hydrogenation of the terminal C=C bond with  $H_2$  catalyzed by the encapsulated Pd nanoparticles.

Finally, the use of bifunctional metal/acid catalysts for multistep reactions has been further explored in **Chapter 5**. To the previous Pd compound, we added new bifunctional MOFs, containing either encapsulated Pt nanoparticles or isolated Pd or Pt complexes attached to the organic linkers of the MOF. We discuss the use of these compounds, and the relevance of the acid properties of the material introduced by the  $Cr^{3+}$  nodes, for the one-pot sequential reduction of nitroarenes and reductive amination of carbonyl compounds. This preparative two-steps reaction has been exploited to synthesize various secondary arylamines, while suitable intramolecular variants have been successfully used to prepare *N*-containing heterocycles: quinolines, pyrroles, and 3-arylpyrrolidines. In all the cases, the MOFs have shown superior performances with respect to commercially available Pd and Pt metal catalysts under the same conditions.