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CTC-PO-04 Role of IRMOF-3 Zn_4O Vertices in Knoevenagel Condensation

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The Knoevenagel (*Knvgl*) condensation, employed to produce alkenes, involves couple of molecules singly having carbonyl groups and α acidic hydrogen atoms. It has been recently reported that the third member of the Isoreticular Metal Organic Framework family (IRMOF-3) [1] may behave as a basic catalyst, active in the *Knvgl* condensation [2]. The lattice structure of this family of solids is based on Zn_4O moieties (inorganic vertices) and poly-topic linkers, derived by functionalizing 1,4 Benzendicarboxylate (BDC) derivatives.

Within the density functional theory (DFT) framework we already studied structural and basic properties of IRMOF-3 derivatives. Moreover, the mechanism of the catalytic cycle for the *Knvgl* condensation of benzaldehyde and ethyl cyanoacetate was analyzed. The investigation of local chemical properties and of a plausible reaction route for the aniline and dimethyl-2-aminoterephtalate (DM2AT) *Knvgl* catalytic condensation has been also performed, in order to clarify the effects of the inorganic vertices on the amine moieties. Aniline and DM2AT, were chosen for modeling the effects of increasing complexity around the basic sites, characterizing the IRMOF-3 system.

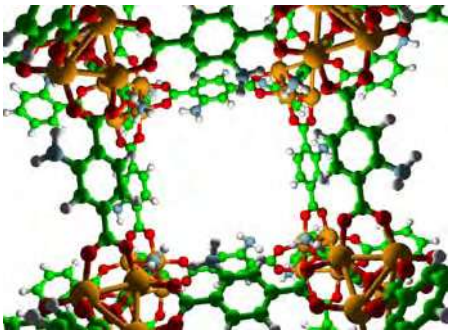

Figure 1. IRMOF-3 cage

The basicity of aniline-like amino moieties grew, along with the catalytic activity, when incorporated into MOF structures. However, the basicity of this class of catalysts did not depend on the charge density present on the nitrogen atom of the aminic group. On the contrary, the basicity was for the most part referable to the IRMOF-3 conjugate acid stabilization, determined by interactions involving the inorganic vertices. Besides this, a direct involvement of the inorganic vertices in the catalytic mechanism could be also pointed out.

These findings, highlighting the active role of the inorganic vertices in the IRMOF-3 activity, are here discussed.

[1] O. Yaghi, M. O'Keeffee, W. Ockwig, K. Chae, M. Eddaouddi and J. Kim, *Nature*, *423*, **2003**, 705.
[2] J. Gascon, U. Atkay, M. Hernandez-Alonso, G. K. F. van Klink, *J. Catal.*, *261*, **2009**, 75.