Catalytic role of UiO-66 and UiO-66-NH_2 in Fischer esterification: a mechanistic study

Chiara Caratelli[1], Julianna Hajek[1], Francisco G. Cirujano[2], Avelino Corma[2], Michel Waroquier[1], Francesc X. Llabres i Xamena[2], Veronique Van Speybroeck[1]

[1]Center for Molecular Modeling (CMM), Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium
[2]Instituto de Tecnología Química, Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos, s/n, 46022 Valencia, Spain

Metal organic frameworks (MOFs) are a class of hybrid materials in which metal ions or metal clusters are connected by organic linkers. They show catalytic properties and can be easily tuned by changing their building units. In particular, UiO-66, a Zr-based MOF, is characterized by an exceptional stability, which arises from its high coordination number. It is known that defects are present in the structure, in the form of missing linkers or nodes, and their number can be tuned by adding modulators during the synthesis [1]. A non-fully coordinated Zr results in a Lewis acid site that can be exploited for catalysis. It has been shown that UiO-66 is an efficient and stable Lewis acid catalyst for esterification with superior results compared to homogeneous catalysts [2, 3]. The catalytic effect increases when this MOF is functionalized with -NH_2, but the role of this group during the reaction is not yet clear. In fact, it has been recently shown that in aldol condensation on the same material the amino group doesn't play an active role but has a stabilizing effect [4]. Moreover, on the UiO-66 metal cluster there are other active sites available for the catalysis which give rise to multiple possible routes for the reaction [4]. In particular, the *oxo*-atoms on the defect site are Brönsted base sites which can take part in the reaction. The possibly adsorbed water on Zr sites could behave as Brönsted acid. Molecular modeling on extended cluster and periodic models would bring insights into the esterification mechanism on UiO-66 and UiO-66-NH_2 and help to understand the behavior of this highly appealing material.

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E-mail: chiara.caratelli@ugent.be
www: https://molmod.ugent.be