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## Zirconium-containing metal organic frameworks as solid acid catalysts for the esterification of free fatty acids: Synthesis of biodiesel and other compounds of interest

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### ABSTRACT

Zr-containing metal organic frameworks (MOFs) formed by terephthalate (UiO-66) and 2-aminoterephthalate ligands (UiO-66-NH<sub>2</sub>) are active and stable catalysts for the acid catalyzed esterification of various saturated and unsaturated fatty acids with MeOH and EtOH, with activities comparable (in some cases superior) to other solid acid catalysts previously reported in literature. Besides the formation of the corresponding fatty acid alkyl esters as biodiesel compounds (FAMES and FAEEs), esterification of biomass-derived fatty acids with other alcohols catalyzed by the Zr-MOFs allows preparing other compounds of interest, such as oleyl oleate or isopropyl palmitate, with good yields under mild conditions.

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### 1. Introduction

Biodiesel [1,2] consists of a mixture of alkyl (methyl or ethyl) esters of long chain fatty acids derived from oils or fats (triglycerides) having properties similar to diesel obtained from oil (gasoil). As compared with diesel derived from petroleum, biodiesel has the main advantage of being biodegradable and its combustion in diesel engines emits less SO<sub>x</sub>, CO, solid particles and organic compounds. Therefore, biodiesel is considered to be in general less toxic than petroleum diesel. The industrial process for the preparation of biodiesel involves the transesterification of triglycerides with methanol or ethanol using stoichiometric amounts of strong Brønsted bases, such as sodium methoxide or sodium/potassium hydroxides [1,2]. However, this process requires raw materials having low water contents to limit catalyst dilution or neutralization with water, along with a low content of free fatty acids (FFA) to avoid the formation of soaps by saponification side reactions. The formation of these byproducts consumes the stoichiometric base, decreases the biodiesel yield and complicates the separation of the esters due to the formation of emulsions.

An alternative route to produce biodiesel compatible with raw materials rich in FFA (i.e. wastes and by-products of industrial biomass processing or from food processing plants [3]) is the direct esterification of FFA with low molecular weight alcohols (methanol or ethanol), as shown in Scheme 1.

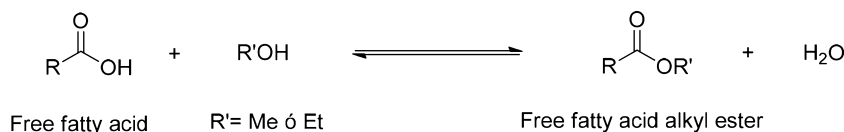
Esterification of carboxylic acids with alcohols can be accomplished by using an acid catalyst that rapidly drives the above equilibrium to the products. Common acid catalysts employed in the biodiesel production include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids [4]. However, the use of mineral acids has serious handling, corrosion and environmental problems. In this sense, active and stable solid acid catalysts appear as an attractive alternative to mineral acids, allowing the easy isolation of the fatty acid alkyl ester products and avoiding corrosion of the equipment.

In recent years, metal organic frameworks (MOFs) have attracted much interest for their potential as heterogeneous catalysts [5–9]. MOFs are crystalline porous solids formed by the linkage of metal ions or metal–oxo clusters and polydentate organic linkers, forming three dimensional networks defining strictly regular nanometric pore channels and cavities similar to those found in zeolites. The large number of available metals and organic molecules that can be used to prepare a MOF leads to a virtually infinite number of possible combinations. This high variability, along with the possibility to introduce new functionalities in a pre-formed MOF by post-synthesis modification [10–12], allow to finely tune the chemical compositions, chemical environment and pore structures of the materials and thus, their reactivity. The Lewis acid catalytic

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**Scheme 1.** General reaction scheme for esterification of fatty acids with alcohols.

properties of MOFs have already been demonstrated for many reactions, including cyanosilylation of carbonyl compounds [13–16], epoxide methanolysis [17], isomerizations of  $\alpha$ -pinene oxide and citronellal [18,19], Friedländer condensation [20], alkene cyclopropanation [21], etc. In many cases, the Lewis acid character of the MOF is induced by the creation of a coordination vacancy upon thermal removal of a solvent molecule ( $\text{H}_2\text{O}$ ) initially bound to the metallic nodes. Recently, Cavka et al. [22] have reported the synthesis of a robust Zr terephthalate MOF, referred to as UiO-66. This material contains Zr hexameric building blocks connected by 12 dicarboxylate ligands, forming a face-centered cubic close packing framework. Several isorecticular materials of the family have been obtained so far by replacing terephthalate ligand by other linear dicarboxylate molecules (such as amino- or nitroterephthalate, or 4,4'-biphenyl dicarboxylate), which allows tuning the dimensions of the pores and the chemical composition of the solid. In spite of lacking coordination vacancies in their ideal crystalline structure, Zr-containing UiO-66 type MOFs [22] also display the typical reactivity expected for a Lewis acid catalyst [23–25]. According to recent characterization studies [26], the catalytic activity of these Zr-MOFs would arise from both the occurrence of a reversible (thermal) dehydroxylation of the  $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$  clusters to  $[\text{Zr}_6\text{O}_6]^{12+}$  exposing  $\mu_3$ -vacancies, together with the systematic formation of crystalline defects associated to linker deficiencies. Very recently, de Vos and co-workers have demonstrated that the amount of missing linkers in the framework (and thus the catalytic activity of the resulting material) can be controlled to some extent by using a modulated synthesis approach with trifluoroacetic acid and HCl followed by thermal activation [27]. Therefore, given the well known Lewis acid character of UiO-66 type materials and their noticeable thermal, chemical and mechanical stability [28], we have anticipated that these materials could make good candidates as solid acid catalysts for FFA esterification for the production of biodiesel and other compounds of interest. In this work, various alcohols have been used along with both, saturated and unsaturated FFA of different chain lengths. Comparison of the results obtained with the MOFs and with other acid catalysts reported in literature is also provided.

## 2. Experimental

### 2.1. Synthesis of the MOFs

UiO-66 and UiO-66- $\text{NH}_2$  solids were prepared according to the reported procedure [29]. Briefly, 750 mg of  $\text{ZrCl}_4$  and either 740 mg of terephthalic acid (UiO-66) or 800 mg of 2-aminoterephthalic acid (UiO-66- $\text{NH}_2$ ) were dissolved in 90 mL of DMF (Zr:ligand:DMF molar ratio of 1:1:220) and the solution was kept in a round bottom flask without stirring at  $80^\circ\text{C}$  for 12 h and at  $100^\circ\text{C}$  for another 24 h in an oil heating bath. The resulting material was recovered by filtration and washed thoroughly with fresh DMF. Then the solid was washed three times by putting it in contact with dichloromethane for 3 h. Finally, the solid was recovered by filtration and dried under vacuum for another 1 h. X-ray diffraction (Phillips X'Pert, Cu K $\alpha$  radiation) was used to confirm the expected crystalline structure of the materials.

Elemental analysis (C, H and N) of UiO-66 and UiO-66- $\text{NH}_2$  was performed on the solids previously degassed under vacuum

at  $150^\circ\text{C}$  for 12 h. Likewise, Zr content in both samples was determined by ICP-OES. For both, UiO-66 and UiO-66- $\text{NH}_2$ , we found higher Zr contents than those expected for the ideal stoichiometric material. These results indicate that linker defects are present in both compounds, as already concluded by others in previous studies [26]. A detailed analysis of the linker deficiency is given in the Supporting Information.

Lewis acidity of the UiO-66 type compounds was evaluated by means of FTIR spectroscopy of adsorbed cyclohexanone. IR measurements were performed on a Nicolet i510 FTIR spectrometer at a resolution of  $4\text{ cm}^{-1}$ . The solids were prepared in the form of thin self-supported wafers of ca.  $10\text{ mg cm}^{-2}$  and degassed at  $150^\circ\text{C}$  overnight under vacuum ( $10^{-3}$  mbar). Then, cyclohexanone vapor was admitted to the cell and, after equilibration, the samples were degassed for 1 h at increasing temperatures (50, 100 and  $150^\circ\text{C}$ ), and IR spectra were recorded after each step.

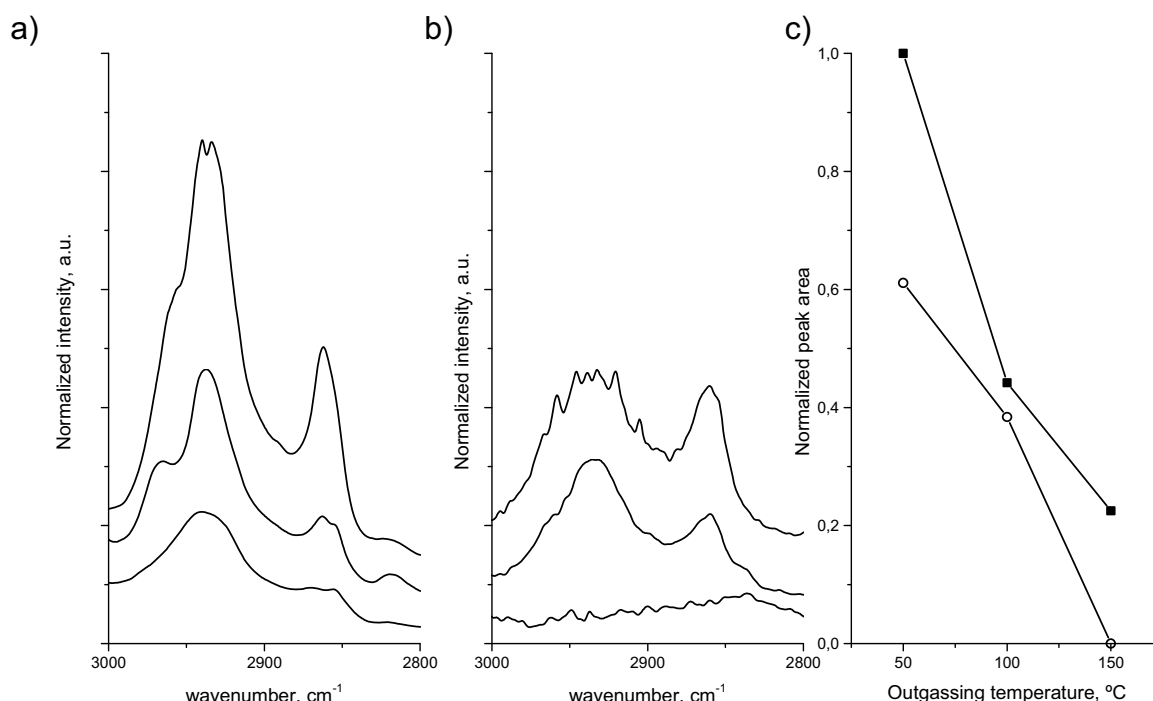
### 2.2. General procedure for esterification reactions

Esterification reactions were performed as follows: 1 mmol of fatty acid, and the desired amount of alcohol were contacted with the MOF (0.07 mmol Zr) in a batch reactor at the specified temperature (see footnotes in the corresponding tables for specific conditions). The reaction was followed by GC-MS (Varian 3900) with a 30 m long and 0.25 mm i.d. capillary column HP-5 (5% phenylmethylpolysiloxane), using dodecane as external standard. Retention times were compared with those of commercial standards. Turnover frequencies (TOFs) of the Zr-MOFs were calculated as moles of product formed per moles of zirconium present in the reaction (considering that all the zirconium atoms of the MOF are participating in the reaction) and per hour. Data were taken at short reaction times corresponding to low levels of conversion (<15–20%).

## 3. Results and discussion

### 3.1. Acid properties of UiO-66 and UiO-66- $\text{NH}_2$

As commented above, the acid character of UiO-66 type materials has been indirectly established for several acid catalyzed reactions [23–25], as well as directly determined experimentally by means of CO adsorption FTIR and microcalorimetry [30], FTIR spectroscopy of adsorbed 5-nonanone [31], temperature programmed desorption (TPD) of  $\text{NH}_3$  [23], and has been theoretically evaluated by DFT [25]. Furthermore, experimental evidences by TPD of  $\text{CO}_2$  [23] and FTIR of adsorbed  $\text{CDCl}_3$  [31] also revealed the presence of basic sites of medium strength in UiO-66- $\text{NH}_2$ , which are absent in UiO-66. In the present work, we have used FTIR spectroscopy of adsorbed cyclohexanone to evaluate comparatively the acid properties of the UiO-66 and UiO-66- $\text{NH}_2$  samples that will be later used in the catalytic studies. Cyclohexanone is a convenient probe molecule to characterize Lewis acidity of solid acids [32,33]. Adsorption of cyclohexanone on Lewis acid sites produces a bathochromic shift of the  $\text{C}=\text{O}$  stretching mode with respect to the value of the free molecule, and the magnitude of the shift depends on the strength of the acid site. Unfortunately, both UiO-66 and UiO-66- $\text{NH}_2$  have strong absorption bands in the region expected for the  $\nu(\text{C}=\text{O})$  mode of cyclohexanone (ca.  $1700\text{--}1670\text{ cm}^{-1}$ ) due to



**Fig. 1.** FTIR spectroscopy of cyclohexanone adsorbed on UiO-66 (part a) and UiO-66-NH<sub>2</sub> (part b) normalized to the Zr amount in each sample. Cyclohexanone was adsorbed at room temperature and desorbed at increasing temperature, at (from top to bottom) 50, 100 and 150 °C. Part c shows the amount of cyclohexanone that remain adsorbed (as normalized intensity of the C–H peaks) as a function of the outgassing temperature on UiO-66 (■) and UiO-66-NH<sub>2</sub> (○).

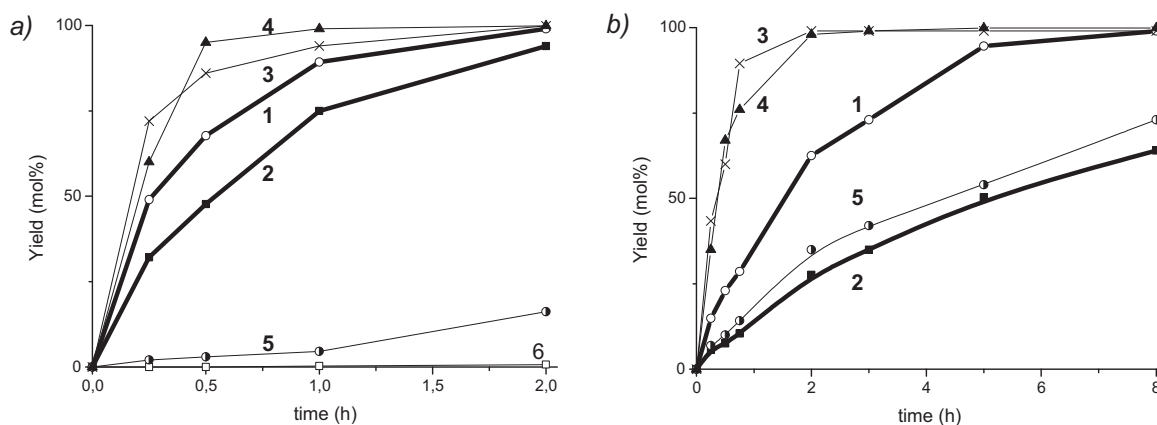
the terephthalate linkers, thus limiting the use of cyclohexanone as probe molecule for this type of compounds. Nevertheless, the Lewis acid strength of the solids can still be inferred from the corresponding C–H stretching modes of cyclohexanone, by evaluating the amount of ketone that remains adsorbed after degassing at a certain temperature. Thus, cyclohexanone was adsorbed at room temperature on previously outgassed samples (150 °C under vacuum overnight), and then desorbed successively at increasing temperatures (50, 100 and 150 °C) for 1 h. The results obtained are shown in Fig. 1, for UiO-66 (part a) and UiO-66-NH<sub>2</sub> (part b), together with the normalized integrated intensity of the C–H stretching bands of cyclohexanone as a function of the outgassing temperature (part c). Note that the spectra in parts a and b have been previously normalized to the zirconium content of the wafer to allow a direct comparison. As it can be seen in Fig. 1, both materials can adsorb cyclohexanone, thus revealing a certain Lewis acidity, though the amount of cyclohexanone adsorbed on UiO-66 is about two times higher than on UiO-66-NH<sub>2</sub> (see Fig. 1c). Furthermore, cyclohexanone is completely removed from UiO-66-NH<sub>2</sub> after outgassing at 150 °C for 1 h, while it still remains a significant fraction of cyclohexanone adsorbed on UiO-66 after the same thermal treatment (ca. 23% of the amount adsorbed at 50 °C). Both results indicate that UiO-66 contains twice as much Lewis acid centers than UiO-66-NH<sub>2</sub>, and their acid strength is higher, in agreement with the conclusions drawn in previous studies [23,30,31].

### 3.2. Esterification of lauric acid (C12) with methanol or ethanol

In order to test the catalytic activity of Zr-containing UiO-type MOFs for the esterification of free fatty acids, we first considered lauric acid (dodecanoic acid, hereafter C12 for short) as model compound, and methanol and ethanol as alcohols. The results obtained for UiO-66, UiO-66-NH<sub>2</sub> (i.e., an isorecticular UiO-66 material built up by aminoterephthalate linkers) and other reference catalysts are shown in Fig. 2 and Tables 1 and 2. In all cases, esterification with MeOH is considerable faster than with EtOH, as expected due to

the higher nucleophilic character of MeOH and the corresponding lower activation energy of the addition step. Blank experiments revealed that these reactions are auto-catalyzed to some extent by the acid reagent, C12, yielding under the reaction condition used up to 56% of methyl laurate and 12% ethyl laurate after 24 h of reaction, respectively (see Table 1, entry 1, and Table 2, entry 1). In comparison, the MOF catalyzed reaction is considerably faster than the auto-catalyzed process (compare entry 1 with entries 2 and 3 in Tables 1 and 2). Additional control experiments in the presence of either terephthalic or aminoterephthalic acid indicates that the contribution from eventual traces of free ligands that might be present in the MOFs is negligible (conversions attained in both cases were practically identical than in the blank experiment).

While both UiO-type materials are active catalysts for C12 esterification with MeOH and EtOH, UiO-66-NH<sub>2</sub> was found to be more active than UiO-66, providing higher turnover frequencies (TOF) and final yields of the ester. In principle, one could expect differences in the acid character of the two materials as a consequence of the electronic effects introduced by the amino groups of the linkers. In this sense, the groups of Ahn [23], de Vos [24,25] and Timofeeva [31] have recently reported the comparative catalytic properties of isorecticular UiOs bearing various functional groups in the terephthalate linkers. According to these authors, the catalytic properties of the UiOs are highly dependent on the acid character of the materials, and this acidity can be modulated by the presence of functional groups in the MOF structure. Thus for instance, according to the kinetic data obtained for citronellal cyclization [25], introduction of electron withdrawing groups in the terephthalate linkers (such as nitro groups) increases the Lewis acid strength of the Zr clusters due to an electronic induction effect, resulting in a higher catalytic activity (with respect to non-functionalized UiO-66). Conversely, the presence of electron donating groups (such as amino groups) produces the opposite effect and, hence, a drop of the catalytic activity. A similar reactivity trend was also observed for benzaldehyde acetalization [31]. However, this is not the reactivity trend that we have observed in the present

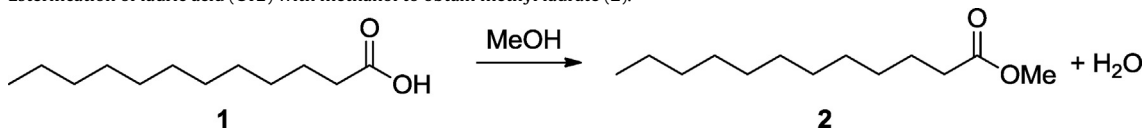


**Fig. 2.** (a) Esterification of lauric acid (C12) with methanol at 60 °C over: UiO-66-NH<sub>2</sub> (curve 1), UiO-66 (2), ZrCp<sub>2</sub>Cl<sub>2</sub> (3), H<sub>2</sub>SO<sub>4</sub> (4), Zr(acac)<sub>4</sub> (5) and tetragonal ZrO<sub>2</sub> (6). In all cases, 8 mol% Zr (or 8 mol% H<sup>+</sup> in the case of H<sub>2</sub>SO<sub>4</sub>) and a C12:MeOH: molar ratio of 1:26 was used. (b) Esterification of lauric acid with ethanol at 78 °C over: UiO-66-NH<sub>2</sub> (curve 1), UiO-66 (2), ZrCp<sub>2</sub>Cl<sub>2</sub> (3), H<sub>2</sub>SO<sub>4</sub> (4) and Zr(acac)<sub>4</sub> (5). In all cases, 8 mol% Zr (or 8 mol% H<sup>+</sup> in the case of H<sub>2</sub>SO<sub>4</sub>) and a C12:EtOH: molar ratio of 1:18 was used.

study for C12 esterification over UiO-66 and UiO-66-NH<sub>2</sub>. Thus, an alternative origin is probably behind the differences in reactivity of the two materials. One possible explanation is that, as pointed out by Morris et al. [34], about one third of the amino groups in the as-synthesized zirconium terephthalate are in the form of protonated  $\text{—NH}_3^+\text{Cl}^-$  salts, formed by the hydrolysis of the ZrCl<sub>4</sub> precursor and HCl released during the MOF synthesis. These highly electronegative  $\text{NH}_3^+$  groups could act as electron withdrawing groups, thus enhancing the Lewis acidity of the zirconium oxoclusters in the same way as NO<sub>2</sub> groups do. In any case, this situation would imply the presence of two coexisting and opposite electronic induction effects acting simultaneously,  $\text{—NH}_3^+$  increasing and  $\text{—NH}_2$  decreasing the Lewis acidity of Zr centers, that would neutralize each other to some extent. Another possible explanation for the higher catalytic activity of UiO-66-NH<sub>2</sub> for C12 esterification could involve the direct participation of the amino groups in the activation of the reaction substrate, by assisting in the activation of the nucleophilic character of the alcohol and elimination of the water molecule. Thus, UiO-66-NH<sub>2</sub> would be acting as a bifunctional acid–base catalyst for the esterification reaction, as shown in Scheme 2. In this dual activation, strong individual acid

or basic sites are no longer needed to attain high activities and selectivities, but rather the reaction is better performed with mild acid–base pairs in close proximity [35–38], such as those present in UiO-66-NH<sub>2</sub>. Thus, our proposal to explain the higher activity of UiO-66-NH<sub>2</sub> with respect to UiO-66 is that the Zr Lewis acid sites (which are present in both UiO-66 and UiO-66-NH<sub>2</sub> as revealed by FTIR spectroscopy of adsorbed cyclohexanone) can adsorb the fatty acid, thus increasing the electrophilic character of the carboxylic carbon atom. Meanwhile, even if the  $\text{—NH}_2$  groups in UiO-66-NH<sub>2</sub> are not basic enough to deprotonate  $\text{CH}_3\text{OH}$  to yield  $\text{CH}_3\text{O}^-$ , they can still form hydrogen bonded adducts, which will increase the nucleophilic character of the O atom of the alcohol, thus favoring the condensation with the activated carboxylic carbon of the fatty acid. In spite of UiO-66-NH<sub>2</sub> having less and weaker acid sites than UiO-66, its higher catalytic activity can be explained by the occurrence of a dual activation mechanism, which make not necessary the presence of strong acid sites. On the contrary, UiO-66 lacking these amino groups, cannot benefit from a dual activation mechanism as must rely only on the Lewis acid sites to catalyze the reaction. The same reactivity trend observed for fatty acid esterification (i.e., UiO-66-NH<sub>2</sub> > UiO-66) was also observed for CO<sub>2</sub>

**Table 1**  
Esterification of lauric acid (C12) with methanol to obtain methyl laurate (2).

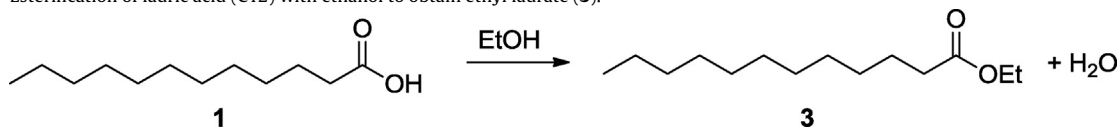


|    | Catalyst                                                          | C12:MeOH molar ratio | <i>t</i> (h) | Temp. (°C) | Catalyst (mol%) | Yield of 2 (mol%) | TOF <sup>a</sup> /Product <sup>b</sup> (h <sup>−1</sup> ) | Reference |
|----|-------------------------------------------------------------------|----------------------|--------------|------------|-----------------|-------------------|-----------------------------------------------------------|-----------|
| 1  | Blank                                                             | 1:26                 | 2 (24)       | 60         | –               | 9 (56)            | –                                                         | This work |
| 2  | UiO-66                                                            | 1:26                 | 2            | 60         | 8               | 94                | 16/6                                                      | This work |
| 3  | UiO-66-NH <sub>2</sub>                                            | 1:26                 | 2            | 60         | 8               | >99               | 25/6                                                      | This work |
| 4  | H <sub>2</sub> SO <sub>4</sub>                                    | 1:26                 | 2            | 60         | 8               | >99               | 30/6                                                      | This work |
| 5  | ZrO <sub>2</sub> (tet)                                            | 1:26                 | 2            | 60         | 8               | <1                | Nil                                                       | This work |
| 6  | Zr(acac) <sub>4</sub>                                             | 1:26                 | 2            | 60         | 8               | 20                | 1/1                                                       | This work |
| 7  | Zr(Cp) <sub>2</sub> Cl <sub>2</sub>                               | 1:26                 | 2            | 60         | 8               | >99               | 36/6                                                      | This work |
| 8  | Zr Oxophosphate                                                   | 10:1                 | 10           | 65         | 5               | 72                | 1.5 <sup>c</sup> /1                                       | [47]      |
| 9  | Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> | 1:6                  | 2            | 100        | 3.2             | 39.4              | –/6                                                       | [48]      |
| 10 | Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> | 1:6                  | 2            | 140        | 9.6             | 95.7              | –/5                                                       | [48]      |
| 11 | Mn(Laurate) <sub>2</sub>                                          | 1:14                 | 2            | 100        | 4               | 19                | –/2                                                       | [49]      |
| 12 | Mn(Laurate) <sub>2</sub>                                          | 1:14                 | 2            | 140        | 4               | 79                | –/10                                                      | [49]      |
| 13 | SiO <sub>2</sub> -SO <sub>3</sub> H                               | 1:35                 | 6            | 65         | 1.4             | 99                | –/12                                                      | [50]      |
| 14 | Halloysite                                                        | 1:12                 | 2            | 160        | 16.3            | 95                | –/3                                                       | [51]      |
| 15 | MoO <sub>3</sub> /SiO <sub>2</sub>                                | 1:12                 | 15           | 120        | 0.4             | 97                | –/16                                                      | [52]      |
| 16 | Bi <sub>2</sub> O <sub>3</sub>                                    | 1:20                 | 2            | 140        | 2               | 65                | –/16                                                      | [53]      |

<sup>a</sup> Turnover frequencies (TOF) cannot be calculated for most of the reactions taken from literature since no conversions at short reaction times were provided.

<sup>b</sup> Productivity of the catalyst, as moles of product formed per mol of catalyst and per hour, calculated at the end of the reaction.

<sup>c</sup> TOF has been estimated from the data shown in Fig. 7 of reference [47].

**Table 2**Esterification of lauric acid (C12) with ethanol to obtain ethyl laurate (**3**).

|    | Catalyst                                                          | C12:EtOH molar ratio | t (h)  | Temp. (°C) | Catalyst (mol%) | Yield of <b>3</b> (mol%) | TOF <sup>a</sup> /Product <sup>b</sup> (h <sup>-1</sup> ) | Reference |
|----|-------------------------------------------------------------------|----------------------|--------|------------|-----------------|--------------------------|-----------------------------------------------------------|-----------|
| 1  | Blank                                                             | 1:18                 | 8 (24) | 78         | –               | 4 (12)                   | –                                                         | This work |
| 2  | UiO-66                                                            | 1:18                 | 8 (20) | 78         | 8               | 64 (80)                  | 2.8/1                                                     | This work |
| 3  | UiO-66-NH <sub>2</sub>                                            | 1:18                 | 8      | 78         | 8               | 99                       | 7.4/1.5                                                   | This work |
| 4  | UiO-66-NH <sub>2</sub> <sup>c</sup>                               | 1:18                 | 8      | 78         | 8               | 60                       | 2.1/0.9                                                   | This work |
| 5  | UiO-66-NH <sub>2</sub>                                            | 1:5                  | 8 (20) | 78         | 8               | 42 (55)                  | 1.5/0.5                                                   | This work |
| 6  | H <sub>2</sub> SO <sub>4</sub>                                    | 1:18                 | 2      | 78         | 8               | 94                       | 17.5/6                                                    | This work |
| 7  | ZrO <sub>2</sub> (tet)                                            | 1:18                 | 20     | 78         | 8               | 7                        | Nil                                                       | This work |
| 8  | Zr(acac) <sub>4</sub>                                             | 1:18                 | 8      | 78         | 8               | 72                       | 3.4/1                                                     | This work |
| 9  | Zr(Cp) <sub>2</sub> Cl <sub>2</sub>                               | 1:18                 | 2      | 78         | 8               | 99                       | 21.7/6                                                    | This work |
| 10 | Zr-Beta zeolite                                                   | 1:18                 | 20     | 78         | 2               | 34                       | <1                                                        | This work |
| 11 | Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> | 1:6                  | 2      | 100        | 3.2             | 23.1                     | –/4                                                       | [48]      |
| 12 | Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> | 1:6                  | 2      | 140        | 3.2             | 77.2                     | –/12                                                      | [48]      |
| 13 | Mn(Laurate) <sub>2</sub>                                          | 1:14                 | 2      | 140        | 4               | 75                       | –/10                                                      | [49]      |
| 14 | SiO <sub>2</sub> -SO <sub>3</sub> H                               | 1:35                 | 7      | 80         | 1.4             | 99                       | –/12                                                      | [50]      |
| 15 | Halloysite                                                        | 1:12                 | 2      | 160        | 16.3            | 87.1                     | –/3                                                       | [51]      |
| 16 | MoO <sub>3</sub> /SiO <sub>2</sub>                                | 1:12                 | 15     | 120        | 0.4             | 95                       | 21 <sup>d</sup> /16                                       | [52]      |
| 17 | HPA/Ta <sub>2</sub> O <sub>5</sub>                                | 1:3                  | 3      | 78         | 0.1             | 65.6                     | –/219                                                     | [54]      |
| 18 | HPA/Ta <sub>2</sub> O <sub>5</sub>                                | 1:9                  | 3      | 78         | 0.1             | 99                       | 800 <sup>e</sup> /330                                     | [54]      |

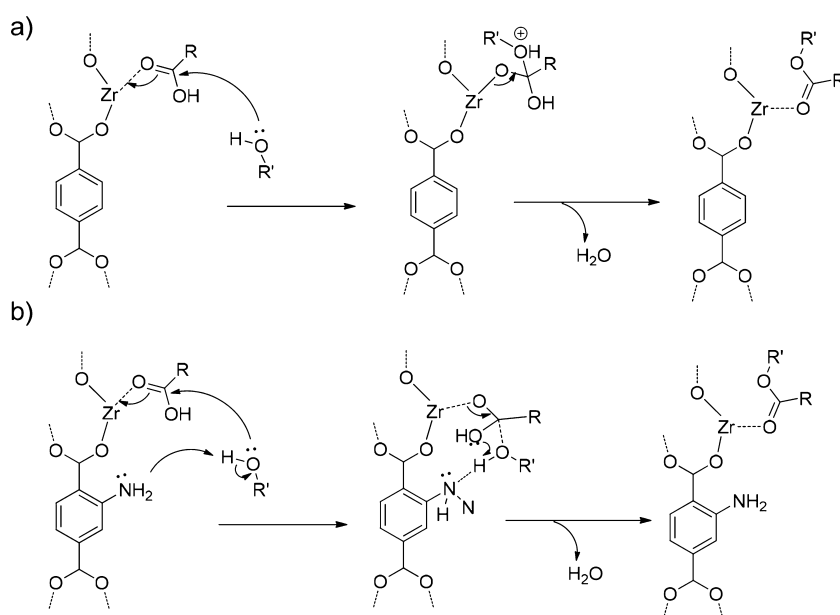
<sup>a</sup> Turnover frequencies (TOF) cannot be calculated for most of the reactions taken from literature since no conversions at short reaction times were provided.<sup>b</sup> Productivity of the catalyst, as moles of product formed per mol of catalyst and per hour, calculated at the end of the reaction.<sup>c</sup> A H<sub>2</sub>O:C12 molar ratio of 15:1 was added at the beginning of the reaction.<sup>d</sup> TOF has been estimated from the data shown in Fig. 6 of reference [52].<sup>e</sup> TOF has been estimated from the data shown in Fig. 8 of reference [54].

cycloaddition to styrene oxide [23] and cross-aldol condensation [24], for which similar acid–base bifunctional mechanisms were proposed.

The stability of the UiO-66 and UiO-66-NH<sub>2</sub> catalysts under the reaction conditions was checked in all cases by comparing the XRD patterns of the fresh materials with those of the solids recovered after the reaction. In all the cases, the crystallinity of the materials was preserved and the intact solids recovered after the reaction can be re-used without significant differences for at least two additional catalytic cycles. Elemental analysis of the catalysts before and after the reaction, revealed the same Zr content, while

analysis of the liquid filtrate after the reaction presented no traces of Zr, evidencing the lack of appreciable leaching from the solid during the reaction. As an example of the recyclability of the UiO materials, Fig. S1 in Supporting Information shows the XRD of fresh and used UiO-66 and UiO-66-NH<sub>2</sub> catalysts, while the corresponding kinetic curves obtained for the esterification of C12 with EtOH over UiO-66 is shown in Fig. S2.

In order to put into perspective our results obtained with the two MOFs, we have studied the esterification of C12 using other acid catalysts (both homogeneous and heterogeneous) under the same reaction conditions. The most representative results obtained



**Scheme 2.** Plausible reaction mechanism for the alcohol esterification reaction over (a) a monofunctional acid catalyst (UiO-66); or (b) a bifunctional acid-base catalyst (UiO-66-NH<sub>2</sub>).

are included in Tables 1 and 2. In our hands, the performances of the Zr-MOFs with MeOH and EtOH were superior to other zirconium compounds and zeolites tested, such as those reported in Tables 1 and 2, and were only surpassed by zircocene,  $\text{Zr}(\text{Cp})_2\text{Cl}_2$ , and  $\text{H}_2\text{SO}_4$ .

On the other hand, the comparison with catalytic data from literature is not straightforward, since in many cases the reaction conditions used (temperature, C12:alcohol ratio and amount of catalyst) are very different. Nevertheless, Tables 1 and 2 also contain data extracted from previous studies using various types of solid acid catalysts. In general, these studies do not provide enough kinetic data to calculate the corresponding turnover frequencies (TOFs), for which conversion at short reaction times is required. Thus, for the sake of comparison, the productivity of the catalyst, calculated at the end of the reaction as moles of product formed per mol of catalyst used and per hour, is provided in Tables 1 and 2. The same calculation has also been extended to the catalysts measured in the present work. In general, the activities of the Zr-MOFs for C12 esterification with MeOH and EtOH are comparable (in some cases superior) to mild acid catalysts and clearly lower than strong acid materials, such as supported heteropolyacids. Note that most of the studies considered in Tables 1 and 2 were carried out at temperatures well above those used in the present study. Hence, given the endothermic character of the esterification reaction, this can explain, in part, the better productivities obtained with these catalysts with respect to the Zr-MOFs.

The esterification of carboxylic acids with alcohol is an equilibrium governed reaction that determines the maximum yield of ester that can be obtained at a given temperature (the presence of the catalyst only lowers the time needed to attain this equilibrium). Therefore, since  $\text{H}_2\text{O}$  is a byproduct of the esterification reaction, reasonably the presence of  $\text{H}_2\text{O}$  in the reaction medium will displace the equilibrium to the left, and less ester will be produced. Thus for instance, when a large excess of  $\text{H}_2\text{O}$  (15 equivalents with respect to C12) was intentionally added, the final yield of ethyl laurate produced after 8 h passed from 99 to 60% (compare entries 3 and 4 in Table 2), resulting in a decrease of the corresponding TOF from 7.4 to  $2.1\text{ h}^{-1}$ . Meanwhile, if the excess of EtOH used is lowered, the equilibrium of the esterification reaction will be less displaced toward product formation. Thus, when the C12:EtOH molar ratio was lowered from 1:18 to 1:5, the final amount of ester formed also decreased, passing from 99% after 8 h to a maximum yield of 55% after 20 h, while the observed TOF was  $1.5\text{ h}^{-1}$  (compare entries 3 and 5 in Table 2).

### 3.3. Esterification of other saturated (C16, C18) and unsaturated (C18:1, C18:2, C18:3) fatty acids

In view of the good catalytic activity and recyclability of UiO-type MOFs for the esterification of lauric acid with MeOH and EtOH, we wanted to investigate the applicability of the MOFs to other biomass derived free fatty acids with longer chain lengths, both saturated and unsaturated. Thus, we extended our study to the esterification with MeOH and EtOH of palmitic (hexadecanoic acid, C16), Stearic (octadecanoic acid, C18), Oleic (*cis*-9-octadecenoic acid C18:1), linoleic (*cis,cis*-9,12-octadecadienoic acid, C18:2) and  $\alpha$ -linolenic acids (*cis,cis,cis*-9,12,15-octadecatrienoic acid, C18:3). For the sake of brevity, the complete catalytic data obtained for each fatty acid and the comparison with other acid catalysts from the literature is provided as Supporting Information (Tables S1–S10).

In order to illustrate the dependence of the chain length and unsaturation degree of the fatty acid on reaction rate, Fig. 3 shows the calculated pseudo-first order reaction rate constants,  $k$ , of esterification of various fatty acids with ethanol over UiO-66- $\text{NH}_2$ . The same tendency was also observed for UiO-66, although this material was in general less active than UiO-66- $\text{NH}_2$  (as already observed

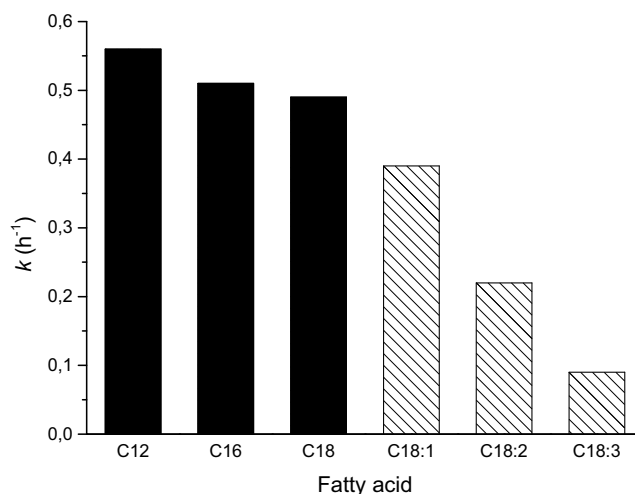


Fig. 3. Pseudo-first order reaction rate constant ( $k$ ) of esterification of various saturated and unsaturated fatty acids with EtOH over UiO-66- $\text{NH}_2$ . (Fatty acid:EtOH = 1:18, 8 mol% Zr with respect to fatty acid,  $78^\circ\text{C}$ ).

for C12 esterification commented above). As it can be observed, the reaction rate decreases as the chain length and the degree of unsaturation of the fatty acid increases. This is probably due to higher adsorption of the unsaturated fatty acid (or fatty ester) on the surface of the solid, which causes the progressive deactivation of the catalyst. However, it is worth mentioning that this deactivation due to product adsorption is fully reversible, and the activity of the catalysts is completely recovered by simply washing with EtOH.

In conclusion, the above experiments demonstrates that both Zr-containing UiOs can efficiently catalyze the esterification of various fatty acids with MeOH and EtOH, being less active as the alkyl chain length and degree of unsaturation of the acid increases. It is also worth mentioning that in all the reactions tested, the Zr-MOFs were found to be stable and reusable without significant loss of activity, as we have previously demonstrated for the esterification of C12 with EtOH over UiO-66- $\text{NH}_2$ .

### 3.4. FFA esterification for the production of other compounds of interest

Thus far, we have demonstrated that Zr-containing UiO-type MOFs can be used as stable and recyclable heterogeneous catalysts for the production of fatty acid methyl and ethyl esters (FAMES and FAEEs) from biomass derived free fatty acids. These compounds form the so-called biodiesel. However, besides the preparation of biodiesel molecules, FFA esterification has interest for the preparation of other compounds that find application as food and cosmetic emulsifiers, lubricants, solvents, surfactants, detergent additives, etc. Herein we will show that UiOs can also be used for the synthesis of valuable chemicals based on esterification of readily available FFAs with various alcohols.

Esterification of fatty acids with long chain alcohols gives high molecular weight esters, known as wax esters. Among them, oleyl oleate, a synthetic analog of jojoba oil, finds application as lubricant for high-speed machinery [39] and is used as base material in cosmetics, pharmaceuticals, paints, wood coatings and perfumery products [40–42]. The results of the esterification of oleic acid with oleyl alcohol to obtain oleyl oleate in the presence of UiO-66- $\text{NH}_2$  are shown in Fig. 4. Analogous results were obtained with UiO-66 as catalyst. As it can be seen in Fig. 4, the presence of the Zr-MOF catalyst clearly improves the esterification reaction and increases the yield obtained with respect to the autocatalyzed reaction. However, when the reaction was performed at  $80^\circ\text{C}$  the time-conversion

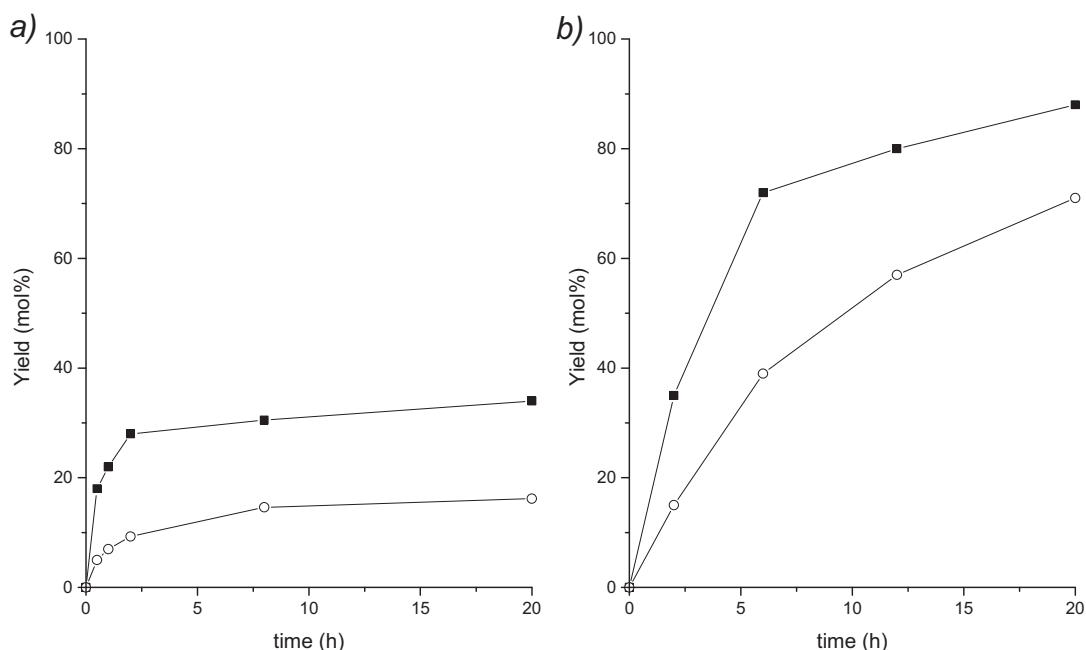


Fig. 4. Esterification of oleic acid with oleyl alcohol at: (a) 80 °C and (b) 110 °C, over UiO-66-NH<sub>2</sub> (—■—) (10 mol% Zr) and in the absence of catalyst (—○—).

plot rapidly reached a plateau and only partial conversion was attained (34% yield after 20 h of reaction). This maximum yield can be increased by slightly rising the temperature to 110 °C (88% yield after 20 h), although in this case the difference with respect to the autocatalyzed reaction was less pronounced. For comparison, Sunitha et al. [43] reported the synthesis of various wax esters using a Lewis acidic ionic liquid catalyst (choline chloride·2ZnCl<sub>2</sub>). Among them, oleyl oleate was obtained in 98% yield after 12 h of reaction at 110 °C, but up to 1 equivalent of catalyst was used (i.e.; 100 mol%, ten times more catalyst than the amount used in the present study). ZrOCl<sub>2</sub>·8H<sub>2</sub>O has also been used as heterogeneous catalyst for the preparation of wax esters, but low yields were obtained in the case of acids and alcohols with chains longer than C14 length [44].

Another product of interest that can be obtained by esterification of free fatty acids is isopropyl palmitate, obtained from palmitic acid and isopropanol. This compound is a dry and soft emollient with good adsorption characteristics used in cosmetics [45], lubricants and is an excellent solvent for mineral oil, silicone and lanolin [46].

In order to determine the applicability of Zr-MOFs for the production of isopropyl palmitate, palmitic acid was contacted with 5 eq isopropanol in the presence of UiO-NH<sub>2</sub> (8 mol%) at 100 °C, and the kinetic data obtained is shown in Fig. 5. Under these conditions, isopropyl palmitate was quantitatively obtained (99% yield) after 20 h, while the blank, autocatalyzed reaction only afforded 9% yield. For comparison, time-conversions attained with other homogeneous (H<sub>2</sub>SO<sub>4</sub>) and heterogeneous (zinc acetate supported on succinic acid-modified SiO<sub>2</sub> as reported in [46]) catalysts are also included in the same plot. As it can be seen, the activity of the UiO material is comparable with that of H<sub>2</sub>SO<sub>4</sub> measured in the same conditions in our lab, while it clearly outperform the results obtained with the supported zinc acetate (although in this case the amount of catalyst used was sensibly lower: 0.2 mol% versus 8 mol% in the present study). In any case, our results demonstrate that UiO-type MOFs can be used as effective heterogeneous catalysts for the production of isopropyl palmitate. The maintenance of the crystalline structure and the fair preservation of the catalytic activity upon reuse indicate that the material can withstand the mild reaction conditions used. In order to determine the full potential of these Zr-containing MOFs, we are currently investigating the

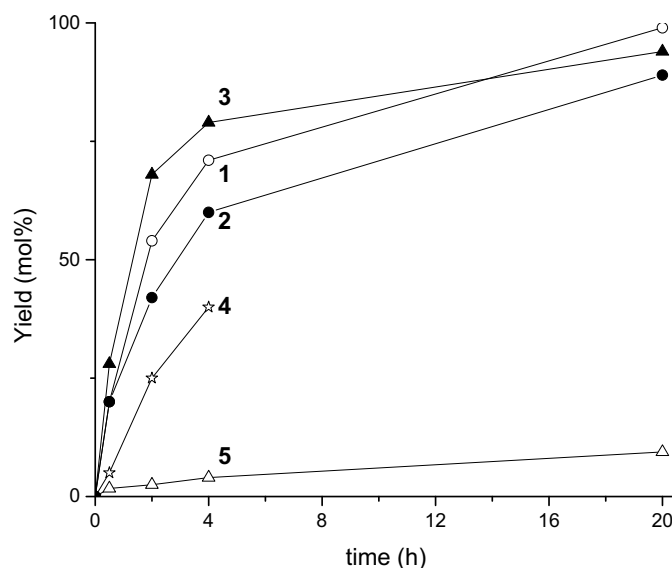


Fig. 5. Esterification of palmitic acid with isopropanol at 100 °C in the presence of various catalysts: (1) UiO-66-NH<sub>2</sub> (8 mol% Zr); (2) reused UiO-66-NH<sub>2</sub> (8 mol% Zr); (3) H<sub>2</sub>SO<sub>4</sub> (8 mol% H<sup>+</sup>); (4) Zinc acetate supported on succinic acid-modified silica (0.2 mol% Zn); and (5) blank experiment, in the absence of catalyst.

long-term stability of the material under continuous operation in a fix bed reactor.

#### 4. Conclusions

In summary, in the present work we have demonstrated that zirconium containing MOFs, UiO-66 and UiO-66-NH<sub>2</sub>, are active, stable and reusable heterogeneous Lewis acid catalysts for the esterification of biomass-derived free fatty acids with various alcohols. The superior activity of UiO-66-NH<sub>2</sub> with respect to UiO-66 indicates the occurrence of a possible cooperative acid–base catalysis, leading to a dual activation of the acid by the coordinatively unsaturated Zr vacancies, along with an assisted deprotonation of the alcohol or water elimination by the amino groups of the

material. Various products ranging from biodiesel compounds (fatty acids ethyl and methyl esters), and other compounds of interest (viz., oleyl oleate and isopropyl palmitate) can be prepared using these Zr-MOFs, with catalytic activities and productivities comparable (in some cases superior) to other solid acid catalysts.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2014.08.015>.

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