MOFs vs Zeolites: carbonyl activation with M(IV) catalytic sites

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The purpose of this perspective article is to compare the catalytic activity of well isolated tetravalent metal sites in microporous zeolites with those present in the oxo-metallic nodes of metal-organic frameworks. Several acid (or acid-base) catalyzed organic transformations of carbonyl containing molecules derived from biomass, relevant for the production of perfumes, flavours and biofuels, will serve as examples for the critical evaluation of the catalytic performance of the M(IV) active sites inside the inorganic (zeolite) or metal-organic (MOF) crystalline framework.

1. Introduction

During the last century, synthetic organic chemistry has helped society providing substances such as fine chemicals in order to satisfy the needs of the chemical industry. A fine chemical is a compound produced in limited quantities as starting material or intermediate for pharmaceuticals, cosmetics or agrochemicals. The high complexity of these relevant organic compounds requires expensive, hazardous and inefficient old-fashion chemical processes with a negative environmental impact. To have a quantitative idea of the low efficiency in the synthesis of fine chemicals, it is estimated that the quantity of toxic residues generated per gram of pharmaceutical is between 20 and 100 times higher. R. Sheldon defines waste as “everything but the desired product”, with the exception of water. One way to quantify the amount of waste produced in a chemical synthesis is by the E (from environmental) factor as the mass of waste divided by the mass of product.¹ Once the waste produced is known, the E factor can be minimized, for instance by using heterogeneous catalysis. Although the amount of chemicals produced in the fine chemical and pharmaceutical industries are relatively not high (compared with bulk chemicals), the E factor is about 1 or 2 orders of magnitude higher. This implies a much higher production of by-products and subsequent isolation and purification steps in fine chemistry related synthetic processes. To achieve a sustainable fine chemicals manufacture, the use of stoichiometric reagents in organic synthesis needs to be substituted by catalysts able to decrease such E factor through the increment in the selectivity to the product of interest. However, due to the small

volumes of the compounds involved and to the use of the least expensive reagent, the implementation of waste reduction in fine chemistry has not been as extensive as in the bulk chemicals related industry. In the last two decades, the use of sustainable catalytic methods in organic synthesis has been an important tool in order to minimize the E factor. Given the solid nature of almost all large-scale industrial catalysts, the use of heterogeneous catalysts for the synthesis of fine chemicals is very appealing. Traditional zeolites or novel (metal)-organic polymers have appear as potential heterogeneous catalysts for these type of processes.^{2,3} This is due to its sponge like porous structures that absorb and concentrate the reagents, favoring the synthetic chemical reactions inside the material pores (stabilizing transition states), which act as microscopic cages with dimensions similar to that of the desired molecules. The use of such solid catalysts facilitates its separation and recovery from the reaction media, avoiding neutralization/separation operations and allowing its reuse in subsequent reaction cycles (depending on the stability of the active sites of the solid). Moreover, the strong interaction between the metal sites and the silica framework (in zeolites) or organic ligand (in MOFs) decreases the leaching of active sites during the reaction.

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Here, zeolites and MOFs porous solid catalysts containing tetravalent metals, M(IV), in its crystalline framework will be compared in terms of activity, selectivity and stability. Special attention will be given to the modification of the physico-chemical properties of the inorganic or hybrid (metal-organic) cavity with the aim to tune the environment of the active site. On the one hand, well-established zeolites will be considered. These are crystalline microporous aluminosilicates with tridimensional structures formed by TO_4 tetrahedra (T= Si or Al) bonded together by oxygen atoms, generating channels and cavities in the order of molecular dimensions. Among them, Beta zeolite is a large pore zeolite formed by twelve member rings with a 6.5 Å pore diameter, in which different metals (Sn, Zr or Ti) has been introduced in framework positions (see Figure 1a). This confers them strong Lewis acidity, needed to carry out different organic transformations with high activity and selectivity towards the desired product.⁴

On the other hand, the aim is to compare the performance of MOFs with traditional inorganic molecular sieves (see Table 1). These hybrid materials are composed of metallic nodes interlinked by organic ligands that form three-dimensional periodic structures with well-defined micropores and pore channels. For instance, the highly stable zirconium terephthalate compound known as UiO-66, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$, H_2BDC = 1,4- benzenedicarboxylate, is a MOF where the terephthalate linkers are coordinated to hexanuclear metallic clusters, generating a face centred cubic framework with a microporous system characterized by two types of cavities of different size: octahedral (11 Å) and tetrahedral (8 Å), which share triangular faces with 6 Å windows (see Figure 1b).^{5a-d} Recently, other Zr MOFs have been described, such as MOF-808 ($\text{Zr}_6\text{O}_5(\text{OH})_3(\text{BTC})_2(\text{HCOO})_5(\text{H}_2\text{O})_2$, H_3BTC = 1,3,5 benzenetricarboxylate), composed of the same secondary building unit (SBU) as the UiO series but with benzene-1,3,5-tricarboxylate (H_3BTC) serving as the organic linker. The tricarboxylate groups link three nodes to each ligand, which creates an open-crystalline structure with pores as large as 18 Å.^{5e-f} Finally, there has also been described the synthesis of a tetracarboxylate highly porous Zr MOFs, such as the NU-1000 ($\text{Zr}_6(\text{OH})_8(\text{OH})_8(\text{TBAPy})_2$, H_4TBAPy = 1,3,6,8-tetrakis (p-benzoic-acid)pyrene.^{5g-i} During the last years, these MOFs have attracted an enormous interest as heterogeneous catalysts, due to its high porosity, crystallinity and stability (respect

Table 1 Chemical and textural properties of the solids discussed

Name	Composition	$\text{ZrO}_2/\%\text{wt}$	$S_{\text{area}}/\text{m}^2\text{g}^{-1}$
Zr-Beta	$(\text{ZrO}_2)(\text{SiO}_2)_{100}^a$	~1-5	~500
UiO-66	$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$	~30-40	~1000
MOF-808	$\text{Zr}_6\text{O}_5(\text{OH})_3(\text{BTC})_2(\text{HCOO})_5$	~30-40	~2000
NU-1000	$\text{Zr}_6(\text{OH})_8(\text{OH})_8(\text{TBAPy})_2$	~30-40	~2000

^a Tentative formula for a Si/Zr ratio of 100. Idem for Sn-Beta

H_2BDC = 1,4- benzenedicarboxylic acid; H_3BTC = 1,3,5 benzenetricarboxylic acid; H_4TBAPy = 1,3,6,8-tetrakis (p-benzoic-acid)pyrene.

to other MOFs); despite its inherent lower thermal and chemical stability compared to zeolites.⁶

This article is focused on reported examples of porous solids (zeolites and MOFs) containing Zr, Sn or other M(IV) catalytic sites for the activation of the carbonyl group of (bio-based) organic molecules enabling a more sustainable synthesis of fine chemicals. In Figure 2 it is summarized the selected transformations of carbonyl containing compounds, i.e. citronellal, glucose and levulinic acid, according to the type of the reaction catalyzed, (i) isomerization, (ii) hydrogen transfer (Meerwein-Ponndorf-Verley reduction or MPV) and (iii) esterification. The nature of the acid sites required for such reactions, either Lewis or Brønsted, is also indicated in the Figure 2, conferring different reactivity towards carbonyl containing molecules. Both types of acid sites, together with basic sites, are present and act as active sites in zeolites and MOFs catalyst. The density and strength of those catalytic sites is dependent on the physico-chemical properties, i.e. chemical composition, porosity, hydrophobicity and defects of the crystalline framework of the zeolite or MOF solids, as will be discuss here.

Figure 1. Isolated Lewis acid sites in the crystalline framework of inorganic zeolite Beta (a) or metal-organic UiO-66 zirconium terephthalate (b). Adapted with permission of references 4g (Copyright 2012, Elsevier Ltd) and 5d. (copyright 2014, American Chemical Society).

Figure 2. (a) Isomerization (carbonyl-ene reaction) of citronellal to isopulegol. (b) Glucose isomerization to fructose and subsequent dehydration to hydroxymethyl furfural (HMF). (c) Levulinic acid esterification to isopropyl levulinate and MPV reduction to γ-valerolactone (GVL).

2. Isomerization reactions

2.1 Citronellal to isopulegol

Many organic synthesis of fine chemicals, such as fragrances, flavours or pharmaceuticals, require isomerization reaction steps catalyzed by Lewis acids. One important fine chemical obtained from terpene precursors is menthol, a natural occurring compound in the essential oil of mint leaves with medicinal, sensory and fragrant properties due to its action within the central nervous system. For its production, the isomerization of citronellal is an important step that must be performed with high activity and selectivity towards the desired isopulegol diastereoisomer, an intermediate in the synthesis of menthol.^{2i,j, 3f}

The Sn-Beta zeolite, having strong Lewis and weak Brønsted acid sites, has been employed for the first time as a substitute of homogeneous ZnCl_2 catalyst for this intramolecular carbon–carbon (carbonyl-ene) bond formation (see Figure 2a).⁷ The stability of the Sn-Beta zeolite makes this catalyst suitable for applications in a fixed bed continuous reactor, not requiring the usual precautions against humidity needed for traditional Lewis acids. Interestingly, the catalytic performance of the Sn Lewis acid sites is superior to other Lewis acids (Ti or Zr) introduced into the zeolite framework (see entry 1 in Table 2). In fact, Ti-Beta gave lower conversion and diastereoselectivity with respect to the isopulegol (compare entries 1 and 2). Moreover, Brønsted-acidic Beta zeolite with a comparable hydrophobicity as Sn-Beta also gave only isomerization without any side-products under the same reaction conditions (entry 3). However, the diastereoselectivity towards the desired isopulegol isomer was low and the conversion only 50% compared to the full conversion obtained with Sn-Beta. The origin of the activity in the Sn-Beta zeolite can be attributed to the tin sites since the all-silica Beta sample has no activity (entry 4). In comparison, the catalytic activity of Zr-Beta for this reaction shows an activity, represented by the turnover frequency (TOF) values calculated as mol of product formed per mol of active site and time, in the same order of magnitude and excellent selectivity (entry 5).⁸ In secondary alcohols as solvent, such as 2-propanol, the selectivity was only 28% because of the Meerwein–Ponndorf–Verley reduction of citronellal to citronellol and subsequent dehydration of the products. The activity of these sites for the catalytic hydrogen transfer will be discussed in the next section. When the catalyst was washed after each reaction with *tert*-butanol, Zr-beta could be reused for several cycles (with no leaching of Zr), recovering the full activity of the catalyst by calcination of the catalyst at 550 °C for 4 h, followed by exposure to ambient conditions overnight.

By experimental and computational studies, De Vos et al. reported that the strength of the Lewis acid sites present in MOFs is directly proportional to the citronellal isomerization activity and isopulegol selectivity (entry 6).⁹ In fact, *the electron-withdrawal effect of the nitro groups in the UiO-66-NO₂, increase the Lewis acid strength of the zirconium sites, enhancing the carbonyl activation step by the strong Lewis acidity of the zirconium active sites.* However, when compared with Lewis acid sites isolated in zeolites, MOF such as the Zr-UiO-66, Cr-MIL-101 or HKUST-1 present much lower activity (up to 2 orders of magnitude).^{3f,10} Therefore, the presence of strong Lewis acid sites in a hydrophobic matrix such as the Sn or Zr in the

Table 2 Isomerization of citronella to isopulegol^a

	Catalyst	Conv. (%)	S _{isopul.} (%)	TOF ^b (h ⁻¹)
1	Sn-Beta	99	83	4600
2	Ti-Beta	35	66	110
3	Al-Beta	50	53	70
4	Pure Si Beta	0	-	-
5	Zr-Beta	69	93	1500
6	UiO-66-NO ₂	99	81	1
7	MOF-808-P	8	85	<1
8	MOF-808-SO ₄	98	55	1
9	H-BEA	95	75	20
10	H-MOR	25	73	1
11	Ir/Beta	90	75	300

^aFor entries 1-4 the reactions were carried out in acetonitrile at 80 °C for 1h.⁷ Entry 5 was performed in *tert*-butanol at 80 °C during 0.25 h.⁸ Entry 6 was done in Toluene at 95 °C for 6h.⁹ Entries 7-8 performed at 60 °C in Toluene for 8h.^{5e} Entries 9-10 were done in cyclohexane at 80 °C for 8h or 2h for entry 11.¹¹ ^bmmols of isopulegol per mmol of active site (Sn, Ti, Zr, Al, Ir) and time, calculated at initial reaction times.

high silica Beta zeolite, favours the rapid formation of the desired isopulegol isomer in comparison with the use of milder Lewis acid metal-organic frameworks. When the Zr(IV) MOF-808-P is treated with aqueous sulfuric acid (MOF-808-2.5SO₄) the selectivity to isopulegol decreases from 85% to 55% due to the strong Brønsted acidity of the MOF, highlighting the importance of Lewis acids for this isomerization reaction (entries 7-8).^{5e} Although, the MOF-808-P shows little activity in this reaction, it is highly active in catalytic hydrogen transfer reactions, as will be shown later on. Moreover, the weak Brønsted acid sites present in the bare Beta zeolite (Si/Al = 11) show remarkable catalytic activity for this reaction. This zeolite needs more time to isomerize quantitatively the citronellal (entry 9), with a TOF in the same order of magnitude as the previously reported by Corma and Renz (compare entries 3 and 9). Also, the presence of Lewis acid sites, i.e. Ir(III), in the Beta zeolite (entry 11) clearly increases the reaction rate.¹¹ Therefore, *the presence of strong Lewis acid sites in a hydrophobic environment is decisive for the high catalytic activity of these Sn or Zr Beta zeolites, compared to MOFs*, as will be confirmed in the following section.

2.2 Glucose to fructose

Another important example of isomerization reaction is the isomerization of glucose to fructose and the further dehydration to hydroxymethyl furfural (HMF), a platform molecule to obtain chemicals and fuels (see Figure 1b).^{12,13} The synthesis of HMF from a renewable source such as the hemicellulose fraction of biomass, allows for the sustainable production of levulinic acid and its esters or even γ -valerolactone, as will be discussed in the next section. While Lewis acid and/or basic sites are required to promote the glucose to fructose isomerization, Brønsted acid sites favours the subsequent dehydration of fructose to HMF. Recently, it has been reported that the Lewis acid sites present in the zirconium-oxo clusters of NU-1000 are active sites for the isomerization of glucose to fructose in water (see entry 1 of Table 3).¹⁴

However, the fructose yield obtained is moderate in contrast with the previously reported when using the Sn-Beta zeolite (compare entries 1 and 3). The reason for the good catalytic performance of Sn-Beta in the glucose–fructose isomerization is attributed to the presence of isolated Lewis acid sites, as described for the citronellal isomerization.¹⁵ In fact, three –OSi and one –OH group bonded to tin in a tetrahedral position of the silica based molecular sieve framework participate in the kinetically relevant intramolecular the rate-limiting step. The hydride shift is controlled not only by the M (IV) active site but also by the basicity of the oxygen atom attached to the metal center. In the case of Sn-Beta, it has been claimed that the adequate polarizability of the active Sn makes the oxygen atom attached to the metal center (–Sn–O–H) a stronger Brønsted base (oxygen with high negative charge) which stabilizes the transition state through electrostatic interactions (see Figure 3a).^{15d,16} In the case of NU-1000, the μ_3 -O oxygen atoms of the oxo-zirconium cluster has been proposed to participate in the proton

Figure 3. Sn–O(H) or Zr–O(H) acid–base pairs present in the inorganic Sn-Beta (a) and metal-organic NU-1000 (b), framework as active sites for the intramolecular hydrogen transfer step in the glucose to fructose isomerization.

transfer steps together with the Zr Lewis acid sites (see Figure 3b).^{14b} One possible explanation to the lower activity of the Zr–O acid–base pairs of NU-1000 with respect to the Sn–O present in Sn-Beta is that *the electron density of the Zr–O bond is less localized on the oxygen, being less basic than the partially hydrolyzed Sn–O–H framework sites in the zeolite.*

When harder Lewis acid sites are incorporated in the zeolite Beta, i.e. Zr^{4+} , Ti^{4+} , it is more likely to suffer competitive adsorption of solvent molecules on the active site because water molecules could coordinate more strongly to a more polarizable center and block them for the adsorption of glucose. Therefore, *sites with strong Brønsted basicity such as Sn–O–H as well as hydrophobic pockets that confine the well-isolated Sn (IV) Lewis acid sites (low amount of defects), leads to turnover rate enhancements with respect to sites isolated within highly defective, hydrophilic molecular sieves.*^{16,17} In Table 3 it is shown that zeolites having a hydrophilic framework showed significantly lower activity per Sn (compare entries 3 and 4). In Zr-MOFs such as NU-1000, the considerable density of highly coordinated Zr oxyphilic nodes $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(OH_2)_4]_8$, either by carboxylates or by water molecules in the NU-1000 solid (see Figure 4), may be another reason for the lower catalytic activity of the hydrophilic Zr Lewis acid sites available with respect to the hydrophobic acid sites present (in low concentration) in Sn-Beta.¹⁸

This highlights the importance of Lewis and Brønsted sites of an adequate strength, in the glucose to HMF isomerization–dehydration two-step tandem process, where each site promote a different type of reaction, isomerization and dehydration, in a sequential mode. In the case of the Sn-Beta zeolite, the lack of strong Brønsted acid sites in the framework favours the glucose–fructose isomerization step but limits its application for the further fructose dehydration step, needing additional catalysts such as HCl. Regarding to the reusability of the catalyst, polymerization of intermediates formed during the reaction lead to the adsorption of carbonaceous deposits in the pores of the catalysts, which poison their active sites. Thus, while the zeolite active sites can be regenerated by a simple thermal treatment,^{13b} for MOFs, the regeneration of the catalysts is limited because of the thermal and hydrolytic stability.

Table 3. Isomerization of glucose to fructose^a

	Catalyst	Conv. (%)	$S_{\text{Fruct.}}$ (%)	S_{HMF} (%)	TOF (h^{-1})
1	NU-1000	60	30	2	<1
2	$\text{PO}_4/\text{NU-1000}$	50	6	15	<1
3	Sn-Beta (Si/Sn=197)	42	67	-	280
4	Sn-Beta- OH-25 (Si/Sn=163)	12	68	-	50

^aFor entries 1 and 2 the reactions were carried out at 140 °C for 5h.^{14a} Entries 3 and 4 were done at 100 °C for 1h.^{15c}

Figure 4. (a) Different hydrophilicity of the active sites present in the Sn-Beta seeds and Sn/deAl-Beta-OH-25 zeolite with “close” and “defect-open” Sn(IV) sites, respectively. (b) The Zr MOF NU-1000 MOF contains a high density of OH/H₂O coordinated Zr₆ nodes (aromatic linkers omitted for clarity). Adapted with permission from references 5g, 15c and 18c. Copyright American Chemical Society.

3. Catalytic hydrogen transfer

3.1 Selective reduction of α,β -unsaturated compounds

An important reaction in the cosmetic, agrochemical and pharmaceutical industries is the reduction of the carbonyl group of ketones to obtain allylic alcohols.¹⁹ Besides catalytic hydrogenolysis with hydrogen as the reducing agent²⁰ an alternative method is the Meerwein-Ponndorf-Verley (MPV) reduction, which traditionally employs an alcohol as a hydride source and metal alkoxides as catalyst.²¹ M(IV) incorporated in zeolites, such as Sn-Beta²² and Zr-Beta²³ are a recognized Lewis acid catalysts for this type MPV reactions. More recently the Zr sites in MOFs have also been able to catalyze the hydrogen transfer from secondary alcohols to carbonyl compounds.²⁴ In order to successfully promote the MPV reduction, coordinative unsaturated Lewis acid sites are required. Those sites activate both the carbonyl group to be reduced and also react with an alcohol reagent, such as *iso*-propanol, to form an activated alkoxide species. Basic oxygen sites in close proximity with Lewis acid sites have been proposed to participate in the reaction mechanism, either with zeolites or MOFs,²⁵ as described for the intramolecular hydrogen transfer step in the isomerization of glucose to fructose (see Figure 3).

The Zr-based MOF-808-P was successfully used as a Meerwein-Ponndorf-Verley chemoselective reduction catalyst for various α,β -unsaturated aldehydes and ketones at 120 °C.^{24b} For cinnamaldehyde, a yield of 99% of cinnamyl alcohol was obtained within a short reaction time. The catalytic activity of MOF-808 is higher than the UiO-66 for this particular reaction (entries 1-2 of

Table 4), although slightly lower than Sn-Beta and Zr-Beta zeolite (entries 3-4). The difference in the catalytic activity of the M(IV) containing solids is mainly related to its Lewis acidity. From the activity decrease in the order: Zr-Beta > ZrAl-Beta > MOF-808 > UiO-66 > Sn-Beta $\approx$ Ti-Beta $\approx$ Si-Beta, it can be concluded that the Zr(IV) sites in framework of zeolite Zr-Beta are strong Lewis acid with high catalytic activity for the hydrogen transfer from the alcohol to the cinnamaldehyde under mild conditions (80 °C and 1h). Under the same conditions, the UiO-66 MOF show less catalytic activity for MPV reactions, in line with their weaker Lewis acidity.

When the amount of Brønsted acid sites is increased by introducing Al in the zeolite framework, the subsequent etherification of cinnamyl alcohol with isopropanol decreases the selectivity towards the allylic alcohol.²³ Interestingly, although Ti and Sn-Beta are active in the reduction of activated carbonyl groups, i.e. 4-*tert*-butylcyclohexanone, no reduction of the more demanding carbonyl group of cinnamaldehyde was observed.^{22a,26} Therefore, the zeolite Zr-Beta shows the higher catalytic activity and Lewis acidity among all the materials tested. Infrared spectroscopy of the solid after adsorption of deuterated acetonitrile (CD₃CN) reveals only one significant band at 2303 cm⁻¹ (Figure 5a), attributed to Lewis acid sites while the other bands at 2275 and 2268 cm⁻¹ are due to acetonitrile H-bonded to silanol groups and physisorbed acetonitrile, respectively. In the case of MOF-808, the catalytic activity may be due, in part, to its open-pore structure (pores of 18 Å), with only six linkers per Zr₆ node. Due to the fact that the reaction occurs at the nodes of the MOFs, which feature a Zr₆(μ_3 -O)₄(μ_3 -OH)₄ SBU, the presence of 12 BDC linkers in UiO-66 fully saturates the coordination sphere of the Zr atoms. The higher amount of Lewis acid sites in MOF-808-P with respect to UiO-66 has been proved experimentally via CD₃CN sorption, where the ratio of chemisorbed molecules on Lewis acid sites to physisorbed molecules is larger for MOF-808-P. Furthermore, a large fraction of the CD₃CN molecules on the Lewis acid sites of MOF-808-P stay chemisorbed upon desorption under vacuum by increasing

Table 4. MPV reduction of cinnamaldehyde^a

Entry	Catalyst	Conv. ^a (%)	S _{Alcohol}	TOF (h ⁻¹)
1	UiO-66	82	95	1
2	MOF-808-P	99	99	13
3	Zr-Beta (Si/Zr=100)	81	99	75
4	ZrAl-Beta (Si/Al=25)	42	64	40
5	Sn-Beta (Si/Sn=100)	0	0	-
6	Ti-Beta (Si/Zr=125)	0	0	-
7	Pure Si Beta	0	0	-

^aEntries 1 and 2 were carried out at 120 °C during 1h (8h for UiO-66) using 37 equivalents of 2-butanol (R = CH₃),²⁴ while entries 3-7 were carried out at 80 °C during 1h using 63 equivalents of isopropanol (R = H).²³

Figure 5. Environment of the Zr active sites and IR of adsorbed CD_3CN in Zr-Beta(Si/Al = 134) (a), MOF-808-P (b) and UiO-66 (c) frameworks. Adapted with permission from references 24b, 27 and 28 (Copyright American Chemical Society).

temperature to 150 °C, indicating a high acid strength with respect to UiO-66 (see Figure 5b and c).

The crystalline structure of MOF-808-P was retained during the reaction and no Zr leaching was detected after a hot filtration test of the catalyst. However, when the used catalyst was washed with ethanol and thermally activated at 150 °C, the conversion drops by 25% in the subsequent reuse. In the case of Zr Beta, some loss in activity also occurred after five cycles, but calcination almost restored the initial activity.²³

3.2 MPV-etherification tandem process

Corma and Renz combined a catalytic hydrogen transfer MPV reaction with a second etherification reaction step in a one-pot cascade in order to obtain the isopropyl 4-methoxybenzyl fragrance compound, starting from 4-methoxybenzaldehyde. While both Zr and Sn substituted Beta zeolites show high catalytic activity for the tandem process, a study of the isolated reactions showed that Zr-Beta was the most active catalyst for the MPV reduction and Sn-Beta was the most active for etherification.²⁹ Recently, new bimetallic Zr(Ti)-NDC (NDC=naphtalenedicarboxylic acid) stable MOFs have been easily prepared by incorporation of titanium(IV) into zirconium(IV)-NDC framework, conferring weak to medium acidity to this porous material.^{24c} The solids have been studied in the same Lewis acid catalyzed Meerwein–Ponndorf–Verley (MPV) reduction–etherification tandem process. Although these MOFs present Lewis acidity, for this cascade process *both the Zr and Sn Lewis acid sites in the zeolite Beta surpass the activity and stability of Zr and Ti MOFs, which show TOF values one order of magnitude lower than those obtained with the Sn and Zr zeolites* (see Table 5).

Table 5. MPV reduction and subsequent etherification^a

	Catalyst	Aldehyde conv.(%)	S_{Ether}	TOF (h^{-1})
1	Zr-Beta(Si/Zr=134)	100	99	80
2	Sn-Beta(Si/Zr=107)	71	99	40
3	Zr(Ti)-NDC-NH ₂	98	99	2

^aReactions were carried out at 100 °C during 8h²⁹ or 21h^{24c}

Recycling experiments with Zr(Ti)-NDC-NH₂ catalyst demonstrate that the crystallinity is totally maintained after the first cycle. Unfortunately, the catalytic activity drops after 5 cycles, since both the conversion and the selectivity to the ether decreases from 90% to 30%. It seems that the water formed during the etherification may poison the MOF catalytic sites that are available to interact with the substrates; in contrast with the water tolerant M(IV) atoms in the high silica zeolite framework, as described earlier for the isometrization of glucose in water (section 2.2).

3.3 Levulinic acid to γ -valerolactone: MPV-Esterification

Catalytic hydrogen transfer has been applied to obtain γ -valerolactone (GVL) from levulinic acid (LA), a biomass derivative.³⁰ GVL could be considered as a sustainable liquid for global storage/transportation and a renewable hydrocarbon resource for energy and carbon-based consumer products.³¹ The production of γ -valerolactone as a renewable feedstock is interesting due its low vapor pressure which reduces volatile emissions and facilitate safe storage. Moreover, GVL has a high chemical stability which avoids its hydrolysis to the acid form under pH-neutral conditions and the formation of peroxides. This properties enhance its general use as fuel additive to produce cleaner-burning fuels,^{31a} or as intermediate in the production of chemicals such as adipic acid,^{31b} valeric acid^{31c,d} 5-nonanone,^{31e} in the composition of biocides^{31f} and as solvent.^{31g}

The interest of using LA as a precursor of GVL is because of the huge availability of such renewable compound which proceeds from the deconstruction of biomass. An alternative to the use of hydrogen gas or formic acid in the synthesis of GVL consist on the chemoselective reduction of the keto group of LA by hydrogen transfer from a secondary alcohol as a hydrogen source through a MPV reaction (see Figure 1 c). The Zr-zeolite Beta is an excellent catalyst for this MPV reduction due to the strong Lewis acidity that provides high activity at low temperatures (entry 1 of Table 6).^{32a} On the one hand, *for samples containing a small number of weak Brønsted sites and a very high Si/Al ratio such as Zr or Sn Beta zeolite, the preferred reaction pathway is the MPV reduction of the keto group in the levulinic acid and subsequent intramolecular esterification to GVL.* The Zr-Beta catalyst was stable when introduced in a packed-bed flow reactor, with no signs of deactivation after 48 h of continuous reaction.

Table 6. Reduction of Ethyl Levulinate with 2-butanol^a

	Catalyst	Conv. (%)	S _{GVL}	TOF (h ⁻¹)
1	Zr-Beta (Si/Zr=100)	97	99	90
2	Sn-Beta (Si/Sn=100)	26	95	5
3	MOF-808	99	85	7
4	UiO-66	43	18	1
5	UiO-66	63	25	1

^aEntries 1-2 were carried out at 110 °C during 5h (R = CH₃),³² entries 3-4 were performed at 130 °C for 3h^{30a} and entry 5 at 150 °C for 4h (R = CH₂CH₃).³³

On the other hand, the presence of Brønsted acid sites associated to Al-OH sites in zeolites decreases the selectivity to the desired GVL (from 99 to 71% for Zr-Beta and Zr-Al-Beta, respectively) due to the favored esterification of levulinic acid with the 2-butanol solvent at 120 °C (see Figure 1c).^{32b}

The Zr MOF UiO-66 is also active in the transesterification of ethyl levulinate (both at 130 and 150°C), due to the bifunctional nature of the Zr sites, able to catalyze the hydrogen transfer and the esterification reaction (see entries 4 and 5 in Table 6). This results in a lower selectivity to GVL, although the UiO-66 resists the reaction conditions after 5 cycles, maintaining its catalytic activity. The crystallinity, particle morphology and porosity were similar to that of the fresh UiO material, although the linker deficiency increases due to the loss of linker during the reaction. MOF-808 has a better catalytic performance for the MPV reaction of LA than UiO-66 (entry 3), as described in section 3.1. The structure and activity of the MOF-808 was practically the same after five reaction cycles, although in this case the surface area decreases from 1450 to 900 m² g⁻¹.^{30a} NH₃-TPD and CO₂-TPD analysis of the MOFs indicate that they possess acidic and basic sites, being the quantity of these sites larger in MOF-808 than UiO-66(Zr). The origin of the acid-base sites, Zr-O-Zr or Zr-OH-Zr, in the metal clusters of the Zr-MOFs is similar to that proposed for the isomerization of glucose to fructose, where the combination of acid and base sites (Zr⁴⁺ and O²⁻) from the metal cluster interact with both isopropanol and ethyl levulinate to form a six membered ring transition state (see Figure 6). The main conclusion of this section is that the reaction rate obtained with Zr-Beta is up to one order of magnitude higher than that obtained with Zr MOFs, probably due to the higher Lewis acidity of the isolated Zr sites in the high silica Beta zeolite. As occurred in the MPV reduction of aldehydes (Table 4), the MOF-808 shows an activity almost ten times higher than that of the UiO-66, and higher than Sn-Beta. Thus, Zr-Beta zeolite and MOF-808 are potential candidates for liquid phase catalytic hydrogenation of keto compounds, showing high stability and adequate regenerability/reusability, especially in the case of the zeolite catalyst. The high catalytic activity of MOF-808 should encourage additional characterization and catalytic studies, to better understand the key factors that influence the catalytic performance of this MOF samples.

Figure 6. Tentative reaction mechanism proposed for the CTH process of levulinate esters to GVL over Zr MOF catalyst, where the Zr-O acid base pairs in the inorganic Zr-oxo clusters located at the nodes of the MOF framework are supposed to be the catalytic active sites. Reproduced with permission of reference 33. Copyright (2017), American Chemical Society.

4. Esterification reactions

The esterification of levulinic acid (LA) produces alkyl levulinates, which are employed as fragrances, flavours and plastiziers. Their low toxicity, flammability and viscosity makes levulinic acid esters adequate additives of diesel and gasoline due to the similar properties to fatty acid methyl esters, but without the inconvenient of low fluidity at low temperatures.³⁴ Although those esters can be obtained from biomass derivatives such as furfuryl alcohol, the majority of catalysts described are poisoned by the adsorption of carbonaceous species that considerably decreases the activity in the subsequent reaction cycles, as described earlier for the synthesis of HMF from glucose (see Figure 7).³⁵

Figure 7. Esterification reactions of bio-based levulinic acid using the desired alcohol (ROH) as a solvent and an acid catalyst (H⁺) in the context of hemicellulose valorisation.

In order to carry out such esterification reactions avoiding corrosion and environmental problems of mineral acids, solid catalysts have been used. A large part of them are Brønsted acid catalysts, i.e. micro/meso zeolites,^{36a} heteropolyacids,^{36b} sulfated oxides,^{36c} acid impregnated clays^{36d} and acidic ion exchange resins.^{36e} In the case of MOFs, Gascon et al. showed that upon treatment with a mixture of triflic anhydride and sulfuric acid, chemically stable MOF structures MIL-101(Cr) and MIL-53(Al) can be sulfated, resulting in a Brønsted acid group attached to the aromatic terephthalate linkers of the structure.³⁷

Different zeolites have been described in literature for the esterification of levulinic acid with *n*-butanol (entries 1-4 of Table 7).^{36a,38} Among them, ZSM-5, presents stronger acid sites than Beta zeolite, due to its higher Si/Al ratio. However, the ZSM-5 is less active in the esterification of levulinic acid with *n*-butanol than BEA zeolite (entry 1 vs. entries 2-3), which has been attributed to diffusional limitations to the small pores and also to the smaller surface area (310 m²g⁻¹) compared to that of Beta zeolite (710 m²g⁻¹). The importance of having strong acid sites for the catalytic activity in esterification reactions is also confirmed by the higher activity of the hierarchical HZSM-5 zeolite (Si/Al=37). The hydrophobicity of the material (indicated by the Si/Al ratio) may favour the condensation reaction, as reported by Kiss et al.³⁹ As the zeolite hydrophobicity increases, the absorption of the water by-product that will lead to deactivation is avoided. However, if the Si/Al ratio is too high, the zeolite may lose its acidic properties. For low Si/Al ratios, water is easily absorbed, blocking the access of the reagents but when the Si/Al ratio is increased, reaction pockets are created inside a hydrophobic environment, as discussed for the glucose isomerization in water (section 2.2).

It is known that in MOFs, some acid sites can be formed just during the reaction and cannot be assessed by experimental techniques before or after the reaction.⁴⁰ However, in the particular case of the Zr MOFs (i.e. UiO-66 type discussed in this article) it has been

Table 7. Levulinic acid (LA) esterification with *n*-butanol^a

	Catalyst	Conv. (%)	TOF (h ⁻¹)
1	H-BEA (Si/Al=12.5)	82	50
2	H-ZSM-5 (Si/Al=15)	31	6
3	H-ZSM-5 (Si/Al=37)	30	20
4	Hierarchical H-ZSM-5 (Si/Al=37)	90	90
5	UiO-66 (13% defects)	99	110 (400)
6	UiO-66-NH ₂ (9% defects)	99	70 (560)
7	<i>p</i> -toluenesulphonic acid	99	400

^aEntries 1-2: *n*-butanol:LA molar ration 7:1, 120 °C, 4h.⁴⁷ Entries 3-4: *n*-butanol:LA molar ratio 4:1, 100 °C, 5h.^{36b} Entries 5-7: *n*-butanol:LA molar ratio 6:1, 120 °C, 4h.^{40b} The TOF in parenthesis is obtained considering only the Zr sites associated to missing linkers (two per each missing linker).

Figure 8. a) TGA of two UiO-66 samples with different water (18% vs 6%) and missing linkers (13% and 2%). b) Dependence of the linker defect content with the catalytic activity for the esterification of levulinic acid with ethanol using UiO-66 (red), UiO-66-NH₂ (blue) and UiO-66-NO₂ (black star).^{40c}

proposed that the linker content determined from the corresponding thermo-gravimetric analysis is generally lower than that expected for the ideal stoichiometric MOF, which indicates the existence of linker defects in the “as-prepared” samples.^{41a} Therefore, linker deficiencies from 2% to 13% were estimated in the case of UiO-66 samples (see Figure 8a). *The catalytic activity for esterification of levulinic acid is proportional to the linker defects content, in the sense that for materials with low linker deficiency the catalytic activity is also low* (see Figure 8b).^{41c} Indeed, if only the zirconium atoms associated to defects (coordinatively unsaturated Zr⁴⁺ ions) are considered as active sites, the TOF calculated when using UiO-66 is similar to that obtained for *p*-TSA (400h⁻¹) in the esterification of levulinic acid with *n*-butanol (entries 5-7 of Table 7).

For the UiO-66-NH₂, the defect content seems to affect less to the catalytic activity for the esterification of levulinic acid with ethanol. In fact, the material with amino groups have a superior catalytic activity compared with UiO-66 (560 h⁻¹ vs 400 h⁻¹), which indicates the existence of other sites that could participate in the reaction mechanism or increment the catalytic activity of the defective sites.⁴² In the case of UiO-66-NO₂, the defect content was very low for all the samples prepared, in line with the lower catalytic activity. However, due to the electron releasing nature of the nitro groups,⁹ this material presents a higher catalytic activity than UiO-66 even containing a low linker deficiency (see Figure 8b). In fact, it is logical that the higher acidity of the nitroterephthalic acid (with respect to aminoterephthalic acid) increases the Zr-O-carboxylate strength, decreasing the number of missing linkers.

Moreover, UiO-66-NH₂ adsorb a higher amount of water than the non-functionalized UiO-66 one, due to preferred amine-water interactions (higher density of hydrophilic sites).⁴³ Also, the presence of a proximal basic site in UiO-66-NH₂, favours the interaction of the water molecule with the Lewis basic oxygen or the amino groups,⁴⁴ or even with NH₃⁺ groups formed due to the HCl generated during the ZrCl₄ hydrolysis.⁴⁵ The coordinatively unsaturated Zr sites in the defective high surface area nano-MOF generates a higher amount of strong Brønsted acid sites when interacting with the protic alcohol or the water molecules, as has been summarized in Figure 9. In fact, *the coordinatively unsaturated*

Figure 9. Proposed interactions between water and defective Zr sites in the UiO-66. (a) The acid-base properties of the oxo-metallic clusters may be tuned by the use of hydrophilic and electro-donating NH_2 or hydrophobic (b) and electro-withdrawing NO_2 functional groups (d) attached to the organic linker.

Zr sites are Lewis acid sites which strongly interact with molecules such as water or monocarboxylate used as a crystal growth modulator (Figure 9a).⁴⁶ These water molecules in the coordinatively unsaturated defects present on the Zr MOF can generate mobile protons (Brønsted sites), resulting in an increased protonic conduction through a Grotthuss mechanism, i.e. $\text{Zr}-(\text{H}_2\text{O})(\text{HOH}^+\text{OH})(\text{H}_2\text{O})$.⁴⁷ The increase in the density (Figure 9b) or strength (Figure 9c) of those sites can be tuned by the functional group present in the benzene ring of the linker, as described for the isomerization of citronellal and epoxide ring opening.^{9,48}

From Table 7 it is deduced that the defective Zr-UiO MOFs are, in general, more active than the zeolites described in the esterification of levulinic acid with *n*-butanol (entries 1-4 vs entries 5-6). Interestingly, the Zr(IV) Lewis acid sites in a high silica Beta zeolite does not improve the activity for the esterification of fatty acids with respect to the defective nano-sized Zr-MOFs, in spite of the high catalytic hydrogen transfer activity.^{41b} This is probably due to the higher density of Zr^{4+} hard Lewis (and $\text{Zr}-(\text{H}_2\text{O})(\text{HOH}^+\text{OH})(\text{H}_2\text{O})$ Brønsted) sites in the defective MOF (~30 wt.% ZrO_2) with respect to the Zr-Beta zeolite (~1 wt.% ZrO_2). Moreover, a novel synthetic approach of Zr-MOFs developed by Luz et al. allows the synthesis of very small and well-dispersed defective MOF nanocrystals within mesoporous silica under very mild reaction conditions.^{49a} This fact increases the amount of available Zr active sites in this hybrid UiO-66/ SiO_2 material (~6 wt.% ZrMOF), boosting its catalytic activity in the esterification of testosterone with respect to Zr-Beta zeolite.^{49b} The hybrid MOF material was used in at least seven reaction cycles, showing only a small decrease in the final testosterone ester yield (from 99 to 77%).

In the case of LA esterification, after each reaction cycle the MOF was regenerated by simple washing with EtOH which allows at least three runs of the used catalysts without apparent changes in the crystallinity. The yield of butyl levulinate decreases only from 99 to 96 %, indicating a good reusability of the material.^{36b} In order to regenerate the Zeolite BEA after 4 h reaction, the catalyst was

reactivated by heating in a stream of air at 400–500 °C for 4 h and then reused for five runs without significant loss of activity or crystallinity. Finally, the hierarchical-HZSM-5 catalyst maintains its activity during five cycles with LA conversion of 98%. The spent catalyst was recovered and subjected to calcination in air at 823 K for 5 h to burn away organics deposited. This regenerated catalyst was reused in subsequent five cycles and was found to remain active with a LA conversion of 98%.

Conclusions and outlook

This article analyze some of the catalytic applications of MOFs and zeolites in selected examples that have in common the activation of carbonyl containing organic molecules derived from biomass resources. The catalytic sites present in the structure of these porous solids are able to selectively convert the desired carbonyl functionality of the reagents into a new one. Those functional groups in the product obtained determine the properties and applications as fragrances (isopulegol or menthol), flavours (menthol, fructose or alkyl levulinates) and biofuels (alkyl levulinates or γ -valerolactone). Examples of active and selective crystalline and porous solids in isomerization, hydrogen transfer and esterification reactions have been discussed, comparing the activity and selectivity of MOFs and zeolites containing tetravalent isolated metals M(IV). Due to the limited thermal and chemical stability of the MOFs, the regeneration and reuse of this type of catalysts still far from the more robust and stable inorganic molecular sieves. Nevertheless, the zirconium carboxylate frameworks discussed here are among the most stable MOFs reported until now, combining a high catalytic activity with the possibility to be regenerated and reused under the mild conditions required in the fine chemistry reactions proposed here. The perspective provided in the text could be summarized in following four main ideas:

- Compared to MOFs, the low amounts of M(IV) catalytic active sites present in the zeolite matrix has been successfully employed for Lewis acid catalyzed reactions such as isomerizations and hydrogen transfer, obtaining higher TOFs than those obtained with MOFs. However, by functionalization of the MOF linker (UiO-66-X, X=H, NH_2 , NO_2 ...) it is possible to tune the Lewis acidity of the Zr sites, controlling the activity and selectivity in isomerization reactions. The electron-withdrawal effect of the nitro groups in the UiO-66- NO_2 , increase the Lewis acid strength of the zirconium sites, enhancing the carbonyl activation step by the strong Lewis acidity of the zirconium active sites of this MOF.
- The nature of the catalytic active site (Ti, Zr, Sn, Hf...), coordination environment (saturated or partially unsaturated) and the polarity, hydrophilicity or hydrophobicity of the framework are important physico-chemical parameters that influences the adsorption of the reactants from the solvent into the active sites. The polarizability of those active sites as well as the participation of neighboring groups in the stabilization of the transition state has been also highlighted here for the activation of carbonyl groups. For the isomerization of glucose to fructose in water, sites with strong Brønsted basicity such as Sn-O-H as well as hydrophobic pockets that confine the well-

- isolated Sn (IV) Lewis acid sites, leads to turnover rate enhancements with respect to sites isolated within highly defective, hydrophilic molecular sieves.
- iii) While M(IV) containing zeolites seems to be more active in isomerization reactions such as citronellal to isopulegol or glucose to fructose, some MOFs shows promising results in catalytic hydrogen transfer reactions using alcohols as hydrogen source. The strong Lewis acidity of the coordinatively unsaturated Zr sites present in the open structure of MOF-808, turns this material into a potential candidate for liquid phase catalytic hydrogenation of carbonyl compounds. Moreover, when both a keto and a carboxylic acid groups are present in the same molecule, i.e. levulinic acid, interesting effects on the selectivity to the esterification or hydrogen transfer reaction pathways are observed when working in an alcohol solvent. On the one hand, for M(IV) zeolites containing a small number of weak Brønsted sites and a very high Si/Al ratio, the preferred reaction pathway is the MPV reduction of the keto group in the levulinic acid and subsequent intramolecular esterification to GVL. On the other hand, the presence of Brønsted acid sites associated to Al-OH sites in zeolites or Zr-(H₂O)(HOH⁺OH)(H₂O) in MOFs decreases the selectivity to the desired GVL due to the favored esterification of levulinic acid.
- iv) Finally, in the case of hydrophilic Zr nanoMOFs, their outstanding catalytic activity due to the Brønsted acid sites associated to water molecules coordinated to Zr(IV) coordinatively unsaturated sites, pave the road towards further research on new catalytic applications of acid MOFs (or MOFs composites) that are robust enough to be shaped for industrial catalytic processes. In this sense, the growth of very small MOF nanocrystals (with a high amount of exposed active sites in the outer surface of the nanocrystal) has been employed in the esterification of levulinic acid, fatty acids or testosterone; obtaining a promising catalytic performance with respect to inorganic (oxides, clays, silica, zeolites) or organic (ion exchange resins) well-established solid acids.
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Acknowledgements

The European Commission-Horizon 2020 under the Marie Skłodowska-Curie Individual Fellowship grant agreement number750391 (Project acronym SINMOF) is kindly acknowledged for financial support.

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