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Hf-based Metal-Organic Frameworks as acid-base catalysts for the transformation of biomass-derived furanic compounds into chemicals

Sergio Rojas-Buzo,[a] Pilar García-García,*[a] Avelino Corma*[a]

Hf-based metal-organic frameworks (MOFs) are reported here as heterogeneous catalysts for the highly selective and efficient cross-aldol condensation of biomass-derived furanic carbonyls with acetone under mild reaction conditions with near quantitative yields. NMR studies with isotopically labeled acetone confirm that acid-base pairs in the MOF framework promote soft enolization of acetone through α-proton abstraction. The catalyst, Hf-MOF-808, can be recycled several times with only a minor decrease in catalytic activity, that could be regained by soxhlet extraction. Furthermore, Hf-MOF-808, maintains activity in the presence of frequent contaminants in biomass-based molecules such as water and acids, unlike traditional base catalysts. Generality of the procedure was shown by accomplishing the transformation with aromatic and aliphatic aldehydes with acetone as the enolizable component to yield the corresponding α,β-unsaturated methyl ketones which are versatile synthons in fine chemistry. Hf-MOF-808 could also be used in the one-pot synthesis of allylic alcohols by sequential aldol condensation reaction to yield the α,β-unsaturated methyl ketone and subsequent Meerwein-Ponndorf-Verley reduction of the carbonyl by a simple solvent exchange from acetone to isopropyl alcohol. Furthermore, Hf-MOF-808 was decorated with palladium particles and the resultant material could be used in the one-pot aldol condensation and subsequent highly selective double bond reduction.

Introduction

Development of efficient processes for the production of liquid fuels and commodity chemicals from biomass is attracting a great deal of interest since biomass appears as a sustainable feedstock.[1-3] Enormous efforts are being made to devise suitable and proficient catalytic reactions, wherein heterogeneous catalysis plays a predominant role for practical and technical reasons.[4-7] While successful transformations have been developed and quite interesting procedures have been found with potential application in a future biomass-refinery, aiming to mimic present oil-refineries, several challenges remain. Probably the most important deals with catalyst deactivation. While most transformations are designed and developed for pure starting materials, it is encounter that sometimes even low amounts of contaminants present in the starting feed bring about catalyst deactivation which consequently requires thorough and costly purification pretreatments. The goal is, therefore, the design and development of new catalysts that could carry out the transformations in a highly efficient and selective manner and that additionally can stand common contaminants making the overall process cost and time effective.

Aldol condensation is one of the most common reactions in organic synthesis, in which two carbonyl-containing compounds are coupled to form a C-C bond via an intermediate enol (or an enolate anion) species to produce α,β-unsaturated compounds after a dehydration step. The transformation has recently awakened considerable interest in the development of biomass-upgrading schemes as a fine strategy to combine small molecules to produce compounds with longer carbon chains and therefore in the fuel range.[8] For example, furfural (C5) and other furanic carbonyls (C6) represent a significant fraction of the thermal decomposition of cellulose and hemicellulose.[9, 10] Acetone (C3) can be produced from the fermentation of glucose.[11, 12] Combination of these components through aldol condensation allows the formation of products in the range of C8-C15 that could be further transformed in liquid alkanes in the fuel range through hydrogenation/dehydration/hydrodeoxygenation reactions.[13]

Aldol condensation can be catalyzed by both acids and bases, being most commonly used base catalysts. Homogeneous bases such as NaOH, Ca(OH)$_2$, KOH are widely used industrially as catalysts for aldol condensation due to their high activity for the transformation and have been tested in the biphasic aldol reaction of furfural and 5-(hydroxymethyl)furfural with acetone.[14] While the utilization of such catalysts raises

a. *Instituto de Tecnología Química, UPV-CSIC, Universitat Politècnica de València Consejo Superior de Investigaciones Científicas. Avenida de los Naranjos s/n 46022 Valencia, Spain. Email: pgargar@itq.upv.es; acorma@itq.upv.es*

environmental and technical concerns such as high operation and separation costs, it was also observed a certain degree of degradation of the starting material 5-(hydroxymethyl)furfural catalyzed by the base, leading to the formation of organic acids that subsequently neutralize the base catalyst.[14] Additionally, the reaction is frequently found not to be selective giving mixtures of mono and di-condensation products since the acetone component presents two enolizable positions. Solid catalysts have many advantages over the homogeneous counterparts such as corrosion free, simple separation, fewer environmental issues, lower separation and maintenance costs and lower energy requirements. Among the solid base catalysts that are active for aldol-condensation of furfural derivatives and acetone are metal oxides,[13, 15-17] and hydrotalcites.[18] However, these solid bases easily deactivate in the presence of acids, such as acetic acid, which are ubiquitous in biomass-processing, and they also exhibit selectivity issues in this transformation giving mixtures of both mono- and di- condensation products in variable proportions.[16, 18] Recently, Lewis acidic zeolites such as Hf-, Sn- and Zr-Beta zeolites have been reported to promote the direct aldol condensation of aromatic aldehydes with acetone and these materials show potential to work under conditions in which many aldol condensation catalysts are deactivated, meaning in the presence of certain amount of water and acetic acid.[19] While Hf and Zr-beta zeolites show good results for the aldol reaction of benzaldehyde with acetone, poorer result is obtained with the biomass-furanic derivative 5-(hydroxymethyl)furfural, achieving a conversion of 73% and good selectivity of >99% for the single cross-aldol condensation product.[19] Even inferior results are obtained with *p*-nitrobenzadehyde with conversions in the range of 38 and 48% for Hf-beta and Zr-beta zeolites, respectively. Furthermore, while the metal (Hf or Zr) loading utilized represents the 2 mol% with respect to the starting (furanic) material, the low metal content present in the zeolite (Si:Hf ratio of 112) implies the utilization of high weight% of the catalytic solid with respect to the starting material, which could hamper practical applications.

Metal-organic frameworks (MOFs) are highly porous, crystalline and three-dimensional reticular structures composed of organic bridging ligands that are coordinatively bonded to metal ions or metal ion clusters.[20, 21] The high metal concentration together with some other interesting properties such as high surface area and porosity, active-site uniformity and well-defined structures make these materials promising candidates for applications in heterogeneous catalysis,[22-26] and particularly for waste biomass upgrading processes.[27] Thermal, chemical and mechanical stability should be another requirement for the catalytic purposes and in this regard, current investigations are focusing on materials that appear resistant to the sometimes relatively harsh reaction conditions needed. Zr-MOFs are characterized by exceptional thermal, chemical, and mechanical stability.[28, 29] Their unique properties make them privileged materials and outstanding candidates in heterogeneous catalysis, finding use either as catalysts or catalyst supports.[30] Due to their exceptional characteristics, Zr-

MOFs have proved to be useful catalysts in biomass conversion schemes and successful applications have been reported such as the transfer hydrogenation of ethyl levulinate to form γ-valerolactone[31, 32] using isopropanol as a hydrogen donor, esterification reactions[33-35] and fructose conversion to 5-(hydroxymethyl)furfural.[36] In the same family are hafnium-based MOFs, which have been recently developed and share properties with zirconium-based MOFs, such as high thermal and chemical stability. Catalytic applications of these materials are less explored than the zirconium counterparts probably because of the later development thereof. However, initial studies in biomass-derived molecules transformations are being performed. MOF NUS-6(Hf) functionalized with sulfonic acid group in the organic linker has been reported for the selective dehydration of fructose to 5-(hydroxymethyl)furfural.[37] In our group, we have studied the catalytic transfer hydrogenation of biomass-derived carbonyls over hafnium-based MOFs with isopropanol as hydrogen donor.[38] We found higher reaction rates for the Hf-MOFs as to compare with the Zr analogs. Good yields were achieved in the formation of valuable alcohols and what it is more, the catalyst shows chemical stability and could be recovered and reused for several reaction cycles with only a minor decrease in catalytic efficiency. As far as we know, these are all of the catalytic applications of Hf-MOFs as heterogeneous catalysts in biomass-based transformations, while Hf-MOFs are also being explored for other catalytic transformations such as the Brønsted-acid-catalyzed regioselective ring-opening reaction of epoxides,[39-41] the 1,4-hydroboration of pyridine[42] and in the thioanisole oxidation with hydrogen peroxide.[43] Catalysis at the linker in Hf-MOFs has also been reported for the hydrosilylation of terminal olefins by a 2,2',2''-terpyridine-iron complex included as a bridging ligands in a Hf metal-organic layered material,[44] and for the conversion of CO_2 and epoxides into cyclic carbonates at ambient conditions by Cu porphyrin included in the Hf-MOF named FJI-H7.[45]

We here show the applicability of these exceptionally stable MOF materials to the highly selective aldol condensation reaction of biomass-derived carbonyls with acetone. It is also demonstrated that such bifunctional acid-base catalysts maintain the activity in the presence of water and also, unlike traditional (solid) base catalysts, in the presence of acidic solutions. Furthermore, Hf-MOF-808 is used here for the first time as catalyst support for palladium particles for the one-pot aldol condensation-double bond hydrogenation reaction, which further increases potential of Hf-MOFs positioning them as attractive heterogeneous catalysts in biomass-based molecule transformations.

Results and discussion

Zr- and Hf-based MOFs in the aldol condensation of furfural with acetone.

For the present study, we have selected several Hf-based MOFs that have been prepared following the recently reported procedures. UiO-66(Hf) was the first Hf-MOF developed;[46, 47] it

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is isoreticular to UiO-66(Zr) and consists of hexanuclear, octahedral hafnium (or zirconium) oxoclusters connected through terephthalate (1,4-benzenedicarboxylate) linkers to form the three dimensional rigid framework with a high degree of topological connectivity (ideally 12-coordination in the metal center) and pore diameters of 8 and 11 Å. It was prepared herein by a solvothermal synthesis following the reported procedure[48] using $HfCl_4$ and terephthalic acid in dimethyl formamide, employing formic acid as modulator to facilitate the construction of the crystalline solid. The related UiO-66(Zr) was prepared using the same synthetic procedure except $ZrCl_4$ was used instead of $HfCl_4$. In this manner, similar degree of defects[48] in both frameworks is anticipated and therefore a fair comparison of metal activity could be assessed. Two other MOFs in the UiO family were evaluated here: UiO-66-NH_2(Hf) features the 2-aminoterephthalate as organic linker and was prepared using the same above mentioned procedure, except that 2-aminoterephthalic acid was used in this case. Finally, UiO-67(Hf) with a biphenyl-4,4-dicarboxylate as organic ligand was synthesized[39] utilizing, in this case, benzoic acid as modulator. Due to the extended length of the bridging linker, UiO-67 materials display higher pore sizes (around 12 and 16 Å) and opening window (8Å) as to compare to the UiO-66 solids (see above). While UiO frameworks present a 12-coordination environment in the metal center, MOF-808 materials have been described recently[49] and showcase a 6-coordination in the metal center, appearing as coordinatively unsaturated centers, with promising catalytic activity. Furthermore, the void space in the framework (pore diameters of 4.8 and 18.4 Å) allows easier accessibility of reactants to the catalytically active sites. 1,3,5-Benzenetricarboxylic acid ($BTCH_3$) is the organic linker utilized in the preparation of both Zr and Hf-MOF-808 materials with the nominal chemical formula $[M_6O_4(OH)_4(BTC)_2(HCOO)_6]$ and were obtained here by means of the corresponding solvothermal process.[39, 49] Octahedral crystals of Hf-MOF-808 were observed by field emission scanning electron microscopy (FESEM) as it is shown in Figure 1. All the MOF materials prepared within this work have been reported previously and characterization data obtained here correlates well with the described data. See the Electronic Supplementary Information (Section 1 in ESI) for characterization details of the MOF solids prepared in this work. Characterization of basic and Lewis acid sites in the solids was done by FTIR spectroscopy using $CDCl_3$ and CD_3CN as probe molecules, respectively (Figures S23 and S24, ESI).

This series of highly crystalline, porous, hafnium-and zirconium-based MOFs have been tested in the aldol reaction of furfural with acetone as the enolizable carbonyl component and also as the solvent. The reaction was followed over time by using gas chromatography (GC) and dodecane as internal standard. Figure 2 shows the kinetic results when the reaction was performed at 100ºC and using 10 mol% loading (based on the metal) of the corresponding MOF catalyst. The highest activity was observed for UiO-66(Hf) exhibiting higher rate (TOF = 9.7 h^{-1}) for the reaction of acetone with furfural to give
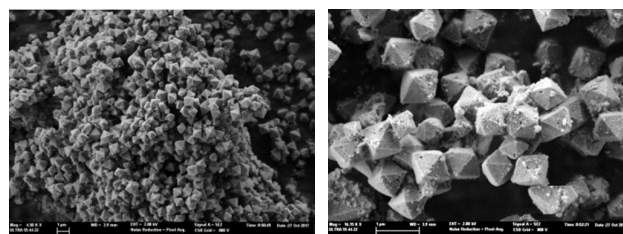

Figure 1. Field emission scanning electron microscopy (FESEM) images of Hf-MOF-808 crystals. Scale bars are included in each micrograph.
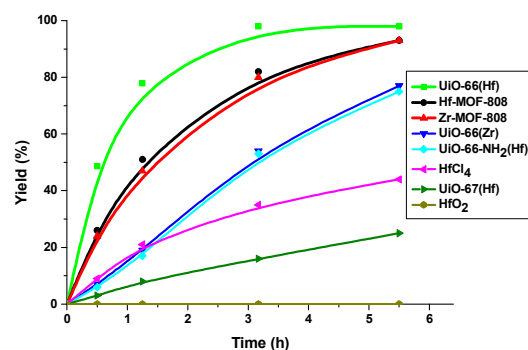

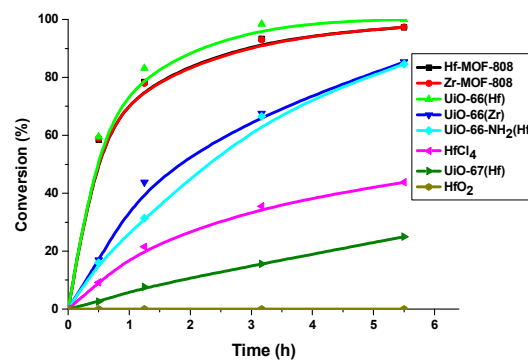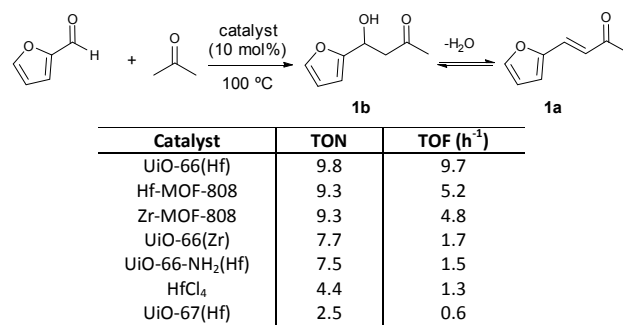| Catalyst	TON	TOF (h^{-1})
UiO-66(Hf)	9.8	9.7
Hf-MOF-808	9.3	5.2
Zr-MOF-808	9.3	4.8
UiO-66(Zr)	7.7	1.7
UiO-66-NH_2(Hf)	7.5	1.5
$HfCl_4$	4.4	1.3
UiO-67(Hf)	2.5	0.6

Figure 2. Hafnium and zirconium catalysts for the aldol reaction of furfural with acetone. Reaction conditions: 0.1 mmol furfural, catalyst (10 mol%), dodecane (10 µL) as internal standard, acetone (0.5 mL), T = 100ºC. TOFs were calculated at initial reaction rate as moles of product formed per hour and per mole of metal site.

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aldol product **1b** and also for the subsequent water elimination step forming the α,β-unsaturated compound **1a**. Lower activity (TOF = 1.7 h^{-1}) is attained with the zirconium counterpart UiO-66(Zr) that would require extended reaction time to achieve good yield of the product under otherwise identical conditions. In the case of MOF-808, both solids, hafnium- and zirconium-based, exhibit similar reaction rates (TOF = 5 h^{-1}), and no reactivity difference can be attributed to the metal employed. It should be notice here that both MOF-808 display similar activity to UiO-66(Hf) in terms of conversion of the starting material while showing lower rate in the dehydration step, although a good yield of 97% of the α,β-unsaturated product can be obtained after 5.5 hours. The transformation appeared quite selective and no other byproducts were detected by GC except for the intermediate aldol **1b**. The double cross-aldol condensation product, difurfuralacetone, was not produced, which is likely attributed to steric hindrance caused by the MOF pore.

The amino-functionalized MOF UiO-66-NH$_2$(Hf) was also tested in the transformation aiming that the combination of Lewis acid and amine base sites resulted in superior performance for the cross-aldol reaction. However, lower rate was observed (TOF = 1.5 h^{-1}) as compared with the amine-free UiO-66(Hf). We hypothesized that adequate distance of acidic and basic sites is encountered in plain MOF UiO-66(Hf) with the Lewis acid site interacting with the carbonyl group of furfural, increasing its polarization and facilitating the attack of acetone, which is enolized by the nearby basic site in the framework in close proximity to the Lewis acid site (Scheme 1). It should be notice that in this study, the MOF catalysts were not pretreated (thermally) before performing the catalytic experiments and therefore the transformation of the Zr$_6$O$_4$(OH)$_4$ unit to the Zr$_6$O$_6$ core in the UiO framework is not occurring as it was reported in the work by De Vos and coworkers.[50] The Lewis acid activity shown here is derived from the framework defects[39,48] due to the use of formic acid in the material's synthetic procedure and also because the coordinatively unsaturated units existing by design in MOF-808 solids.[49] In the case of UiO-67(Hf), benzoic acid was used as modulator instead of formic acid in the preparation method, which could be related to the observed reduced activity
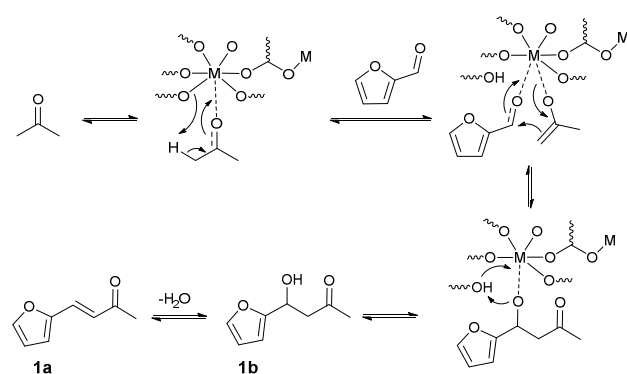
Scheme 1. Aldol reaction of furfural with acetone. Plausible mechanistic pathway catalyzed by Hf- or Zr-MOFs.

(Figure 2) in the catalytic reaction as compared with UiO-66(Hf), since the amount of defects in the framework should differ. The aldol reaction was also tested with HfO$_2$ that displayed no activity in the reaction of furfural and acetone under otherwise similar conditions. For comparative purpose, the homogeneous catalyst HfCl$_4$ was employed, which showed poorer activity (TOF = 1.3 h^{-1}) compared to most of the MOFs shown above (Figure 2). Hence, good results were attained with UiO-66(Hf) and with Hf- and Zr-MOF-808 that are found highly active catalysts for the cross-aldol condensation of furfural with acetone under mild reaction conditions.

Mechanistic studies using NMR spectroscopy and isotopically labeled acetone

NMR studies were next conducted using isotopically labeled acetone to study the extension of the enolization through α-proton abstraction promoted by the acid-base pairs in the frameworks. Scheme 1 shows the proposed mechanism, in which the metal center polarizes the carbonyl group of acetone, acidifying the α-proton facilitating its abstraction by the framework oxygen atom bound to the metal center. The framework oxygen atom is acting as a base, thereby generating a metal enolate that undergoes C-C coupling with aldehydes. Deuterated acetone was used for ^{1}H NMR studies on the reversible keto-enol tautomerization in the presence of several Hf- and Zr-MOF solids. *tert*-Butanol was also employed in the proton exchange experiment. As shown in Scheme S1 in the ESI, a mechanism proceeding via a metal enolate using fully deuterated acetone would result in the transfer of an α-deuterium to the MOF framework that would readily scramble in the presence of unlabeled hydroxy groups such as that one in *tert*-butanol. Due to the reversible keto-enol equilibrium, this pathway would lead to the consecutive replacement of deuterium atoms in [D$_6$]acetone for protons.

The ^{1}H NMR spectra (Table S13, ESI) shows that after heating [D6]acetone at 100ºC for 6 h in the presence of Hf-MOF-808 and *tert*-butanol, it progressively loses its isotopic labels since α-proton signals appeared around 1.95 ppm. A blank experiment was run in the absence of the MOF under otherwise identical reaction conditions that barely showed scrambling in [D6] acetone measured by the use of toluene as internal standard. The ability of several MOF solids to facilitate enolate formation of acetone was then evaluated by means of these ^{1}H NMR spectroscopy experiments (Table S13, ESI). It was found that UiO-66(Hf) provokes superior scrambling of [D6] acetone compared to all the other MOFs tested. This fact can be associated to a higher efficacy in enolate formation. While many other factors are indeed involved in this catalytic procedure such as Lewis acidity of the material, accessibility to the active sites, void volume in the open framework and surface interactions among others, this efficient ability in enolizating acetone could in part explain the superior activity observed for this particular MOF in the aldol condensation with furfural. In line with this, analysis of the basicity of Zr and Hf-based MOFs by FTIR with a probe molecule such as CDCl$_3$ showed, in the difference FTIR spectra, two bands (2278 and

2253 cm^{-1}) for the Zr and Hf UiO-66 solids which evidence the presence of two different basic sites in these frameworks, while only the band at 2253 cm^{-1} is observed for the MOF-808 materials (Figure S23, ESI).[38]

Hf-MOFs tolerance to various contaminants in the aldol condensation of furfural with acetone.

In view of the good results attained in the aldol condensation of furfural and acetone, we were intrigued by the performance and stability of these MOF catalysts in the presence of common contaminants of biomass-based molecules, such as water or acidic solutions. Water can react with many homogeneous Lewis acids interfering in the catalytic procedure due to preferential reaction of the Lewis acids with water rather than the substrates and, consequently, many Lewis acids must be used under strictly anhydrous conditions. Acids contaminants may deactivate strong base catalysts frequently used in aldol condensation reactions. Thus, MOFs catalysts were tested in the presence of these components for the aldol condensation of furfural and acetone (Figure 3). We found that activity of UiO-66(Hf) was severely affected by the presence of excess amount of water (i.e., a molar ratio of 60:1 water:furfural, 10 wt% water) and the conversion decreased by 90% when running the experiment during the same time of 5.5 hours giving mainly the aldol product **1b**. Reaction rate was significantly diminished and the desired condensation product **1a** was formed in only 15% yield after extending the reaction time to 22 hours. On the contrary, Hf-MOF-808 was quite tolerant to the presence of water (again 10 wt% of water was used, what is a molar ratio of 60:1 water:furfural), although conversion decreased by 25% when compared to the dry reaction, the aldol condensation still proceeds and the condensation product **1a** could be obtained in good yield of 76% after prolonging the reaction time to 22 hours (Figure 3, B). It should be noted that dehydration step is still occurring even in the presence of such excess amount of water. With these results, we could conclude that Hf-MOF-808 is far more tolerant to water than zeolite Hf-Beta[19] in similar aldol condensation of benzaldehyde with acetone. The authors also observed that zeolite Hf-Beta maintains activity in the presence of 10 wt% of water, although in their case, conversion was decreased by 50% when compared to the water-free reaction. Next, the activity of MOFs catalysts in the aldol reaction of furfural and acetone was evaluated in the presence of organic acids such as acetic acid. While the commonly used solid base catalyst MgO completely loses activity in the presence of even small quantities of acetic acid (0.06 wt%), both Hf-based MOFs UiO-66(Hf) and Hf-MOF-808 were not quenched by higher amounts of this organic acid (0.22 wt%, i.e. a molar ratio of 4:10:1 acetic acid:substrate:Hf). It was found again that UiO-66(Hf) was more sensitive to the contaminant that provokes a drop in conversion by 76% when running the reaction for the same time (5.5 hours). The decrease in catalytic activity was lower for Hf-MOF-808 (40% decrease in conversion when using 0.22 wt% acetic acid) that tolerates the presence of double amount of acetic acid as

compared with Hf-Beta zeolite, in where 0.11 wt% of acetic acid decreased the conversion by 35%.[19] In any case, both MOFs are active in the presence of the acidic conditions and high yields of 98 and 70% of the condensation product **1a** are obtained with Hf-MOF-808 and UiO-66(Hf), respectively, after prolonged reaction time of 22 hours (Figure 3 C) as determined by GC-analysis. The solid catalysts recovered after the experiments presented a light yellow color that could be attributed to adsorbed furfural degradation products that could be formed in small percentage under the reaction conditions. We believe that the higher tolerance to contaminants exhibited by Hf-MOF-808 compared to UiO-66(Hf) could be related to the framework structures. The lower connectivity of Hf-clusters in Hf-MOF-808 together with the presence of larger apertures facilitate mass transport and allow a better exchange of contaminants (small molecules employed in excess here) with starting material that are all competitors for the same active site. We have also analyzed the resistance of Hf-MOF-808 to monotopic acids such as acetic acid and have evaluated if such contaminant could damage the solid by losing part of its organic linkers by exchange under the reaction conditions. If this would occur, it would ultimately lead to catalyst degradation. In this manner, Hf-MOF-808 was treated in
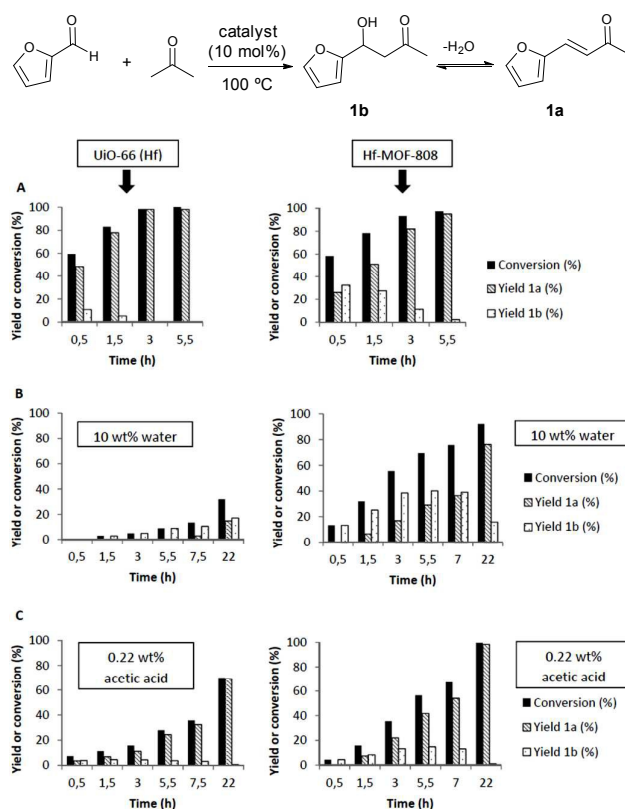

Figure 3. Effects of B) water and C) acetic acid on the aldol condensation of furfural and acetone with catalysts UiO-66(Hf) (left column) and MOF-808-Hf (right column). Reaction Conditions: A) 0.1 mmol furfural, catalyst (10 mol%), dodecane (10 μL) as internal standard, acetone (0.5 mL), T = 100ºC. B) H$_2$O (10 wt% with 600:10:1 water:substrate:Hf molar ration) was also added. C) Acetic acid (0.22 wt% with 4:10:1 acetic acid:substrate:Hf molar ratio) was also added.

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acetone at 100ºC for 24 hours in the presence of several amounts of acetic acid (0.22 wt%, i.e. a molar ratio of 4:1 acetic acid:Hf, 11 wt%, i.e. a molar ratio of 200:1 acetic acid:Hf and 22 wt%, i.e. a molar ratio of 400:1 acetic acid:Hf). The recovered Hf-MOF-808 was then characterized by XRD that showed that the material retains its crystallinity. Additionally, the reaction mixtures were analyzed by gas chromatography wherein no trace of the organic linker 1,3,5-benzenetricarboxylic acid was detected, evidencing robustness of the solid even in the presence of high amount of acetic acid. We conclude thereof that Hf-MOF-808 stands out as a good catalyst for the aldol condensation of furfural with acetone under mild reaction conditions that allows the presence of usual contaminants encounter in biomass strains giving good yield of the desired condensation product (Figure S25, ESI) and, hence, further experimentation and activity evaluation was performed for this particular MOF material.

Catalyst heterogeneity and reusability

The heterogeneity and stability of Hf-MOF-808 was next evaluated by the hot filtration text and the catalyst was removed from the reaction mixture after 30 minutes reacting at 100ºC. Then, the aldol condensation was allowed to procced with the filtrate for 5 additional hours. Results in Figure 4 show that no further reaction is occurring after filtration and, therefore, Hf-MOF-808 behaves as a heterogeneous catalyst and leaching of active species is not taking place. The stability of the catalyst for the aldol condensation of furfural with acetone was also probed by reusing the solid with fresh solutions for five consecutive runs (Figure 4). While the yield remained constant in the first and second runs, a decrease by approximately 12% in conversion was observed for the rest of the recycles, along with a drop in selectivity to the final product **1a** due to the presence of aldol product **1b**. This indicates that a decrease in the rate of alcohol dehydration has occurred (Figure 4, B). The recovered Hf-MOF-808 after five cycles was characterized by FTIR, XRD and ICP and elemental analysis (Figures S26-S28, Tables S14-S15, ESI) and data indicate that the catalyst was stable under the reaction conditions. However, the recovered catalyst after 5 runs presented a light yellow color that together with results from elemental analysis (see Table S14) would indicate deposition of organic-components attributed to furfural degradation occurring to a small extent. With our experience with Hf-MOF-808 as catalyst in the transfer hydrogenation reaction of carbonyl compounds (specifically, with furfural as starting material),[38] we found a substantial decrease in the Brunauer-Emmett-Teller (BET) surface area after repeated use of the material in that reaction, which was attributed to deposition of organic-components that could account for the observed diminished activity in subsequent runs. It was inferred that similar situation could be occurring in the aldol condensation reaction, and therefore soxhlet extraction was performed after run number 3. Indeed, catalytic activity was regained, and a

yield of 94% of the desired product **1a** was again achieved (Figure 4, C).

Scope of the aldol condensation reaction with acetone

Since Hf-MOF-808 exhibited remarkable activity in the aldol condensation of furfural and acetone and additionally may allow the presence of contaminants in the starting materials, the study was expanded to a variety of biomass-derived carbonyl compounds (Table 1, entries 2 and 3). High reaction efficiency was also achieved with 5-(hydroxymethyl)furfural and 5-methylfurfural that gave the condensation products **2a** and **3a** in 91 and 89% isolated yields, respectively, while the selectivity toward the desired single cross-aldol condensation product remained over 90%. Other aldehydes were tested in the procedure. As an example, benzaldehyde can be converted to the benzalacetone **4a** in excellent isolated yield of 94% (Table 1, entry 4). Substitution in the aromatic ring was also allowed and *p*-nitrobenzaldehyde afforded the corresponding condensation product **5a** in 92% isolated yield in only 3 hours reaction time (Table 1, entry 5), while 4-hydroxybenzaldehyde requires longer time (36 hours) to achieve the product **6a** in good isolated yield of 89% (Table 1, entry 6). The reaction was also tested with aliphatic aldehydes such as octanal (Table 1, entry 7). Remarkably, under identical conditions, the much more challenging enolizable aliphatic aldehyde gave the corresponding enone **7a** in excellent isolated yield of 93% and with excellent selectivity since no aldehyde's auto-condensed product was detected by gas chromatography. In all the cases, the *E/Z* ratio of the enone double bond was >95:5 as determined by ^{1}H NMR spectroscopy.
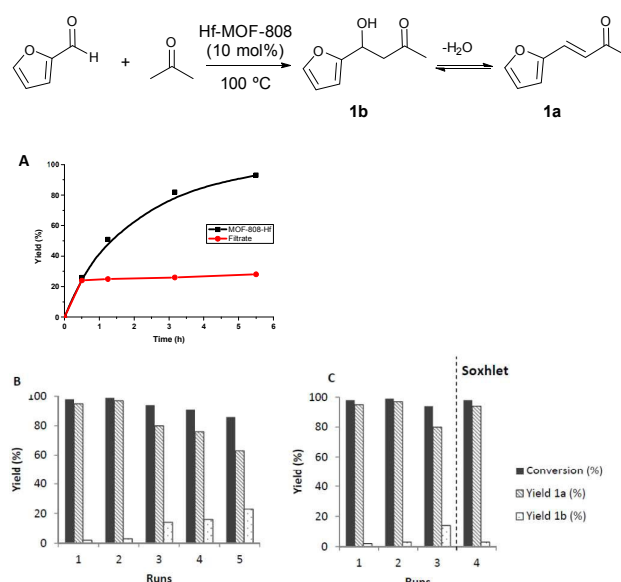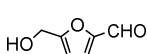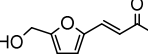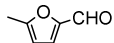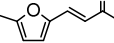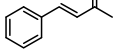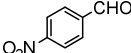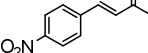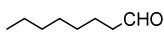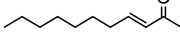

Figure 4. A) Time-yield plots for the aldol condensation of furfural with acetone with Hf-MOF-808 (black line) and remov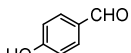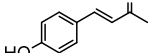ing the catalyst after 30 min (red line). B) and C) reusability of the catalyst. Reaction conditions: 0.5 mmol furfural, Hf-MOF-808 (10 mol%), dodecane (40 μL) as internal standard, acetone (2.5 mL), T = 100ºC, 5.5 hours reaction time. C) Soxhlet extraction with ethyl acetate was performed in the solid catalyst after run 3.

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Table 1. Aldol reaction of several aldehydes and acetone with Hf-MOF-808.[a]

| Entry	Starting Aldehyde	Product	Time (h)	Yield (%)[b]
1		**1a**	12	92
2		**2a**	9	91
3		**3a**	24	89
4		**4a**	24	94
5		**5a**	3	92
6		**6a**	36	89
7		**7a**	48	93

[a] Reaction conditions: 0.5 mmol of aldehyde, Hf-MOF-808 (10 mol%), acetone (2.5 mL), T = 100ºC. [b] Isolated yield after column chromatography.

Two-step one-pot transformation of aldehydes to allylic alcohols

An example illustrating the potential applicability of our method for a two-step, one-pot reaction is shown in Scheme 2 for the synthetic preparation of allylic alcohols. Allylic alcohols are important and versatile intermediates in fragrance and pharmaceutical chemistry.[51] A convenient route for their preparation is via chemoselective reduction of the corresponding unsaturated aldehyde or ketone that in turn are available from many sources such as the aldol condensation reaction among others. Since Hf-MOF-808 appears as a good catalyst for the aldol reaction and also for the transfer hydrogenation of carbonyl compounds,[38] it was employed in the preparation of allylic alcohols starting from aldehydes such as benzaldehyde (Scheme 2), first subjecting it to aldolization reaction with acetone, as shown above, followed by a transfer hydrogenation step using isopropanol as hydrogen donor that is accelerated by the same catalyst.[38] Accordingly, after the first reaction step is completed, acetone was distilled off and isopropyl alcohol was added to carry out the second transformation. We found that the corresponding allylic alcohol was formed in excellent 91% yield (Figure S29, ESI).

Hf-MOF-808 as support for palladium catalyst.

To further expand the versatility and applicability of Hf-based MOF catalysts, we considered the utilization of the solid
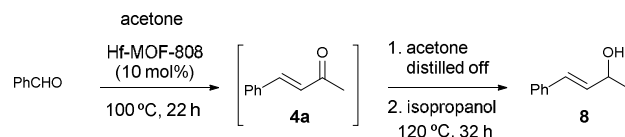
Scheme 2. One-pot synthesis of allylic alcohol **8** with catalyst Hf-MOF-808. Reaction conditions: 0.1 mmol of benzaldehyde, Hf-MOF-808 (10 mol%), acetone (0.5 mL), T = 100ºC, 22 h. Solvent was then evaporated in *vacuo*. Isopropanol (0.4 mL) was then added and dodecane (10 μL) as internal standard, T = 120ºC, 32 hours.

material as support for palladium catalyst. It was envisaged a multifunctional solid with multipurpose catalytic applications and particularly for one-pot synthetic procedures. This research was further justified in the way that aldol condensation of biomass-based carbonyls is frequently coupled with a subsequent hydrodeoxygenation or hydrogenation step either to directly produce liquid alkanes in the fuel range[13, 52-55] or to simply reduce the enone double bond for further applications in heterocyclic ring opening reactions,[56, 57] respectively. To conduct these reactions, noble metal catalysts such as Pd and Pt could be utilized. The idea of combining both, aldol catalyst and Pd (or Pt) catalyst, in a single solid material[17] appears, therefore, highly attractive with process intensification advantages. The utilization of MOFs as supports for metal nanoparticles has been a topic of interest in recent years[58] and yet Hf-based MOFs have been so far elusive in this matter, as far as we know. We have realized the inclusion of palladium species during the MOF synthetic procedure with the utilization of a small amount of palladium acetate in the synthetic gel. Since dimethylformamide is the solvent employed in the MOF preparation, it appeared also useful for our means of forming *in situ* the Pd species (by a dimethylformamide reduction method),[59] which would be trapped inside the MOF pores during its synthesis. The utilization of low amount of palladium would facilitate its extended distribution along the material. A similar concept has been used by our group for the preparation of Pt containing zeolites.[60] The solid here obtained was characterized by an array of techniques such as FTIR, XRD, HRTEM, ICP analysis and N2 physisorption isotherms (Figures S30-S35, Tables S16-S17, ESI). ICP analysis reveals that palladium content is 1.2 wt%. X-Ray diffraction pattern of Pd@Hf-MOF-808 (Figure S30, ESI) show equal reflection bands as bare Hf-MOF-808, which evidence that the palladium precursor is not affecting the synthesis or crystallinity of the final material. Furthermore, no trace of the typical peaks of palladium nanoparticles was observed. Similarly, FTIR spectrum of Hf-MOF-808 and Pd@Hf-MOF-808 appeared practically identical (Figure S24, ESI). Textural properties were also analyzed by means of N2 adsorption isotherm (Figure S35, ESI) and it was found that Pd@Hf-MOF-808 has a BET surface area (500 m^2g^{-1}) in the same range as bare Hf-MOF-808 obtained within these studies (458 m^2g^{-1}) which indicates that palladium is not blocking the pores and it may be in the form of very small particles. HRTEM images of Pd@Hf-MOF-808 (Figure S31, ESI) did not reveal recognizable Pd nanoparticles, presumably too small (TEM detection limit~ 1 nm). Analysis of these images also visualizes

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the lattice fringes of the net confirming its retained crystallinity (Figure S31, ESI). Although a highly crystalline solid was obtained as determined by XRD analysis and also by TEM, it was also observed some amorphous solid that is found surrounding the octahedral crystals of Hf-MOF-808 (see Figures S32 and S33, ESI). STEM imaging and its corresponding EDX elemental mapping for Hf and Pd elements (Figures S32 and S33) show that Pd is located preferentially in that amorphous solid that is found surrounding the octahedral crystals of Hf-MOF-808.

Pd@Hf-MOF-808 in the hydrogenation reaction of enones.

Pd@Hf-MOF-808 was next tested as catalyst for hydrogenation reactions. Benzalacetone **4a** was chosen as model substrate and it was found that double bond can be reduced at atmospheric pressure of hydrogen when using only 0.5 mol% of palladium loading (Scheme 3). The reaction appeared quite selective with the reduction of the double bond and 4-phenylbutan-2-one **9** was isolated in excellent yield of 95%. The reaction was followed over time, and it was also evaluated the heterogeneity of the palladium catalyst by means of the hot filtration test, wherein was concluded that no active species were leached to the reaction medium (Scheme 3). Additionally, the solid was reused for five consecutive runs with equal performance (4 hours reaction time, over 90% yield of **9** as determined by GC using dodecane as internal standard). The postreaction solutions, from the five runs, were combined together and it was analyzed by inductively coupled plasma (ICP) spectrometry and the Hf and Pd content were determined to be 3.7 and 7.3 ppm respectively, further indicating material integrity under the reaction conditions after repetitive use.

Pd@Hf-MOF-808 in the two-step one-pot aldol condensation-hydrogenation sequence and reusability.
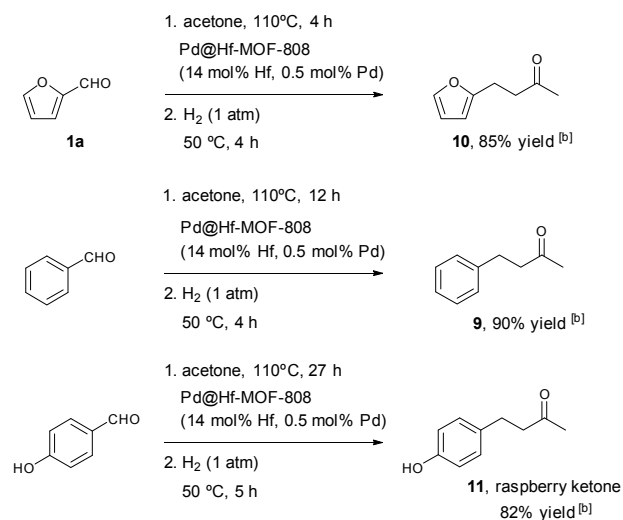
Application of Pd@Hf-MOF-808 in a one-pot two-step sequence was next demonstrated (Scheme 4). Firstly, the aldol condensation of aldehydes with acetone takes place, followed by double bond hydrogenation of the obtained enone by simply applying hydrogen at atmospheric pressure. A similar concept has been used before by our group with a Pd catalyst
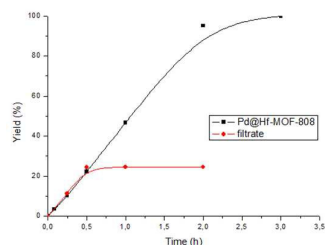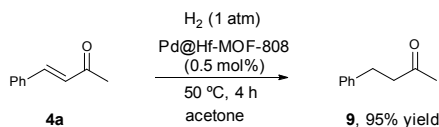
supported over nanocrystalline MgO applied in a one-pot reaction for the production of nabumetone.[61] In the case of furfural, both reaction steps proceeded smoothly and the 4-furanyl-2-butanone product **10** was isolated in 85% yield after column chromatography. The reaction appeared highly selective as determined by gas chromatography, and reduction of the heterocyclic ring was not observed in the crude reaction mixture. The sequence was proved for other substrates such as benzaldehyde that afforded 4-phenyl-2-butanone **9** in high yield of 90% after purification by column chromatography. Raspberry ketone **11**, is the primary aroma compound of red raspberries and it is an important industrial product with antifungal, antiobesity and cardioprotective activities.[62-64] Its synthesis holds interest[65, 66] and it was also obtained here using Pd@Hf-MOF-808 catalyst starting with 4-hydroxy benzaldehyde by the aldol condensation-double bond hydrogenation one-pot sequence. In this way, raspberry ketone **11** was isolated in good yield of 82% and the method further stands out as an appropriate strategy for the preparation of important intermediates and final compounds in fine chemistry.

More importantly, Pd@Hf-MOF-808 could be reused at least five times in the one-pot sequence aldol condensation-hydrogenation reaction (Scheme 5). Performance of the catalyst was similar in the first and second run. However, reaction time was required to be extended for the aldol condensation step in subsequent runs in order to achieve full conversion to the enone product before the hydrogenation step. Nevertheless, catalyst performance for the hydrogenation step was similar for all the five runs.

Scheme 3. Time-yield plots for the hydrogenation reaction of enone **4a** using Pd@Hf-MOF-808 as catalyst (black line) and removing the catalyst after 30 min (red line). Reaction conditions: 0.5 mmol enone **4a**, Pd@Hf-MOF-808 (0.5 mol% in Pd), dodecane (40 μL) as internal standard, acetone (2.5 mL), H_2 balloon (1 atm), T = 50ºC, 4 hours.

Scheme 4. One-pot synthesis of 4-aryl-butan-2-ones with Pd@Hf-MOF-808. Reaction conditions: 0.5 mmol of aldehyde, Pd@Hf-MOF-808 (14 mol% Hf, 0.5 mol% Pd)), acetone (2.5 mL), T = 110ºC. Reaction time as indicated in the arrow. Then, H_2 balloon (1 atm), T = 50ºC, 4 hours [b] Isolated yield after column chromatography.

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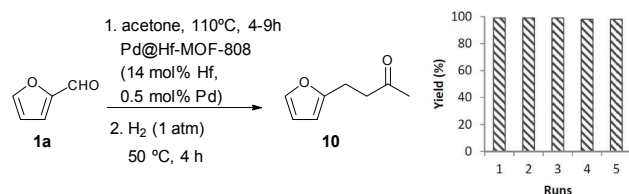
Scheme 5. Reusability of the catalyst in the one-pot synthesis of 4-aryl-butan-2-ones with Pd@Hf-MOF-808. Reaction conditions: 0.5 mmol of aldehyde, Pd@Hf-MOF-808 (14 mol% Hf, 0.5 mol% Pd)), acetone (2.5 mL), T = 110ºC. Reaction time: 4 to 9 hours. Then, H$_2$ balloon (1 atm), T = 50ºC, 4 hours.

After the five cycles, the catalyst Pd@Hf-MOF-808 was recovered and characterized by FTIR, XRD, ICP and elemental analysis and N$_2$ physisorption measurements (Figures S36-S28, Tables S18-19, ESI). The obtained data indicate that the solid material was stable under the reaction conditions. It was observed a reduction in the BET surface area together with an increase in the organic content (elemental analysis), which was attributed to the deposition of organic components which would account for the observed diminished activity after repeated use and the required extended time in the aldol condensation step from run number 3. The reused catalyst, Pd@Hf-MOF-808, was also characterized by STEM and elemental mappings showing that aggregation of Pd has not occurred after successive use of the material in the one-pot two-step sequence. In line with this, typical peaks of palladium nanoparticles were not observed in the XRD pattern.

Conclusions

We have demonstrated that Hf-based metal-organic frameworks (Hf-MOFs) exhibited remarkable activity in the aldol condensation of biomass-based carbonyl compounds and acetone as enolizable component. Hf-MOF-808 appears particularly promising since it can work in the presence of contaminants with which many aldol condensation catalysts are deactivated. The substrate scope could be extended to aromatic and aliphatic aldehydes providing the corresponding enones in good yields with high selectivity towards the mono condensation products. NMR studies confirm that the MOF framework promotes soft enolization of acetone, thus generating a metal enolate intermediate that can attack a carbonyl group to form a C-C bond. An aldol condensation-transfer hydrogenation sequence has been developed to give the corresponding allylic alcohol in good yield. In addition, Hf-MOF-808 was found as a robust support for palladium particles and the resultant solid Pd@Hf-MOF-808 could be used in hydrogenation reactions and also in the one-pot aldol condensation-double bond hydrogenation cascade sequence. These catalysts, Hf-MOF-808 and Pd@-Hf-MOF-808, show chemical stability and could be recovered and reused for several reaction cycles with only a minor decrease in catalytic efficiency that could be regain by soxhlet extraction.

Conflicts of interest

There are no conflicts to declare.

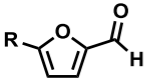## Acknowledgements

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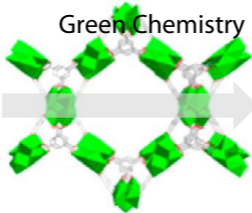66. M. J. Climent, A. Corma, S. Iborra and M. Mifsud, *Adv. Synth. Catal.*, 2007, **349**, 1949-1954.

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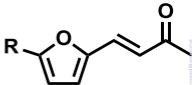
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