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Additional Information

Anion exchange and catalytic functionalization of the zirconium based metal-organic framework DUT-67

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Abstract

A post-synthetic treatment with diluted solutions of the inorganic acids HCl or H_2SO_4 was applied to functionalize the eight connected Zr-based metal-organic framework DUT-67 (DUT - Dresden University of Technology). During the treatment, it is possible to remove and exchange the pristine modulator (formate) by Cl^- or SO_4^{2-} anions. The position of the chlorine in the crystal structure of DUT-67 after treatment could be determined by single crystal X-ray diffraction analysis. Moreover, with the acidic treatment, the polarity of the network as well as its Brønsted acid strength are increased, which have a crucial impact on the catalytic performance. The improved catalytic activity of the acid treated materials was demonstrated in the esterification of levulinic acid with ethanol.

Introduction

Metal-organic frameworks (MOFs) are discussed as materials of high potential for a broad range of applications, such as gas storage,[1-6] separation processes[7-17] or sensor applications,[18-25] mostly because of the high porosity and modularity of the structure. The catalytic activity of MOFs was recognised very early, and up to now MOFs have been applied as heterogeneous catalyst in a broad variety of catalytic reactions.[26-31] Most notably, MOFs bearing open metal sites, such as HKUST-1,[32-37] MIL-100[38-40] or MIL-101[40-42] are ideal Lewis-acid catalysts. But also MOFs, with saturated coordination environment, based on Zr- and Hf-cluster (*e.g.* UiO-66[43]), turned out as active catalyst because of high concentration of defects in this type of materials.

The majority of Zr-based MOFs contain Zr_6- octahedra as inorganic building blocks, where the triangular faces are alternately capped by μ_3-O and μ_3-OH groups. The edges of the octahedron are coordinated to twelve carboxylate linkers creating a coordinatively saturated cluster. The catalytic activity of such materials relies on defects created by missing linkers. Therefore, the concentration of active sites as well as the activity varies from batch to batch.[44-52] As usual, the catalytic activity of a MOF can be tuned either by linker- or by cluster modification. The introduction of electron-withdrawing groups into the linker positively influences the Lewis acidity of the MOF. For instance, by the introduction of the NO_2 group into UiO-66, a 56-fold increase of the conversion rate of the cyclization of citronellal to isopulegol could be achieved.[53] Also

additional Brønsted acid sites could be introduced into the framework by functionalization (e.g.-SO$_3$H or similar groups), expanding the field of potential applications.[54,55]

In the synthesis of Zr-based MOFs, modulators (monocarboxylic acids) are usually used to increase the crystal size of the resulting MOFs and in some cases to reduce the connectivity of the metal cluster.[56] The modulator supported synthetic approach has been demonstrated to control the amount of defects to some extent.[52,57,58] Nevertheless, Zr based MOFs based on clusters with reduced connectivity should give a better level of controllable catalyst structure and tunability. One of the MOFs where the cluster connectivity is only eight instead of twelve is DUT-67, with the composition M$_6$O$_6$(OH)$_2$(tdc)$_4$(Fa)$_2$ (M – Zr or Hf, tdc - 2,5-thiophenedicarboxylate, Fa - formate) (Fig. 1a).[59] The charge balance is achieved by coordination of mono-carboxylate anions (modulator used in the synthesis), OH groups and the linker molecules. Such cluster configuration is ideally suited for the post-synthetic functionalization approach, since the anions can be easily exchanged by other anions in the synthesis or post-synthetically.[60-63]

With the aim to tune the catalytic properties of DUT-67, herein we study the functionalization and anion exchange by post-synthetic treatment of MOF with diluted inorganic acids, since the high stability of Zr-based MOFs against acids is widely reported in the literature.[62,64] As a result of such treatment in DUT-67, the pristine modulator anions (Fa$^-$) are replaced by Cl$^-$ or SO$_4^{2-}$ anions, respectively. The catalytic properties of the new catalysts in comparison to the pristine material were studied in a model reaction, the esterification of levulinic acid, known to be catalyzed by Brønsted acids. The esterification of levulinic acid in the presence of a suitable solid acid heterogeneous catalyst yields ethyl levulinate as the main reaction product, a compound recently reported as a potential biofuel.[65]

Experimental part

General remarks

The metal precursors (ZrCl$_4$ (98% purity) and HfCl$_4$ (98 % purity)) and the linker (2,5-thiophenedicarboxylic acid (H$_2$tdc) (99% purity)) were purchased from Sigma Aldrich. The *N,N*-dimethylformamide (DMF) (p.a. purity) and ethanol (99 % purity) were purchased from ABCR GmbH and the *N*-methyl-2-pyrrolidone (NMP) (99% purity) from ACROS Organics. All chemicals were used without further purification.

Nitrogen physisorption measurements were performed on *BELSORP-max* apparatus *(MicrotracBEL,* Japan*)* and on NOVA 4000e surface area & pore size analyser (*Quantachrome Co.*) at 77 K up to 1 bar. Water vapour physisorption measurements were performed on *Hydrosorb 1000* apparatus (*Quantachrome Co.*) at 298 K up to 1 bar. Prior the adsorption measurements the samples were degassed in vacuum at 373 K for 16 hours.

The thermogravimetric analysis (TG) and differential thermal measurements (DTA) were performed in air on a *STA 409 PC Luxx* (*Netzsch*) thermal analyser with a heating rate of 2 °C/min in a range from 25 °C to 1000 °C. C, H, N elemental analysis was performed using CHNS 932 analyzer (*LECO*).

The powder X-ray diffraction data were collected on a *STOE STADI P* diffractometer with Cu-Kα1 radiation (λ = 1.5405 Å) at room temperature. ^{1}H-NMR spectra were performed on a Bruker DRX 500 P at 500.13 MHz. The spectra were referenced against deuterated DMSO.

MOF synthesis

DUT-67(M)_HCOOH

In comparison with the synthetic procedure reported in ref. [66], the formic acid was used as modulator instead of acetic acid. In a typical synthetic procedure, $ZrCl_4$ (1.38 g, 6 mmol) or $HfCl_4$ (1.92 g, 6 mmol) was dissolved in 150 mL of DMF/NMP mixture (1:1) by ultrasonication for 10 minutes. Afterwards, 2,5-thiophenedicarboxylic acid (0.66 g, 4 mmol) was added and the mixture was sonicated again for 5 minutes. Then formic acid (26.8 mL, 120 eq) was added and the resulting mixture was placed into an oven for 48 h at 80 °C. The white precipitate was filtered off and washed several times with DMF and ethanol. The samples were dried in vacuum at 120 °C. Yield: 89 %.

The composition of the sample was derived from combined data obtained from elemental analysis, TGA (Figure S1 - S6, Table S1, ESI) and ^{1}H NMR after sample digestion (Figure S16 -18, Table S5, ESI).

The elemental analysis for $Zr_6O_6(OH)_2(tdc)_4(HCOO)_2(DMF)_2$ calc.: Zr 34.33, C 24.11, O 30.11, H 1.64, S 8.05, N 1.76; found: C 24.26 H 1.46 S 8.08 N 1.84.

Anion exchange: Synthesis von DUT67_HCl and DUT-67_H₂SO₄

150 mg of as made DUT-67_HCOOH were suspended in 5 mL of HCl or H_2SO_4 solution (of a 2 wt.%) at room temperature for 4 hours. Afterwards the resulting products were washed several times with ethanol and activated in vacuum at 100 °C for at least 12 hours.

The elemental analysis for $Zr_6O_4(OH)_4(tdc)_4(Cl)_4(DMF)(EtOH)_2$: calcd. %: C 22.34, H 1.87, S 7.69, N 0.84, Cl 8.51; found, %: C 22.40, H 2.34, S 8.23, N 0.72, Cl 8.89.

$Hf_6O_4(OH)_4(tdc)_4(Cl)_4(DMF)_{2.5}(EtOH)_2$: calcd. %: C 18.54, H 1.82, N 1.52, S 5.58, Cl 6.16; found %: C 19.11, H 1.26, N 1.55, S 6.34, Cl 6.15

The elemental analysis for $Zr_6O_2(OH)_6(tdc)_4(SO_4)_3(DMF)(EtOH)_2$: calcd. %: Zr C 20.51, H 1.83, S 12.36, N 0.77; found %: C 20.38, H 2.03, S 12.35, N 0.63.

The elemental analysis for $Hf_6O_2(OH)_6(tdc)_4(SO_4)_3(DMF)(EtOH)_2$: calcd. %: C 15.92, H 1.42, N 0.60, S 9.60, found %: C 16.26, H 1.77, N 0.69, S 9.81

Catalysis

Esterification reactions were performed as follows: 1 mmol of levulinic acid (LA), and 0.6 mL of ethanol (15 mmol) were contacted with the MOF (0.018 mmol of either Zr or Hf) into a batch reactor at 80 °C. The reaction was followed by GC–MS (Varian 3900) with a BP20(WAX) column (15 m long, i.d. 0.32 mm) using dodecane as internal standard and comparing retention times with those of commercial standards.

Single crystal X-ray diffraction

The octahedral single crystal of DUT-67(Zr)_HCl with size dimensions of 20 x 20 x 20 µm was placed into a boron-silicon glass capillary 0.3 mm in diameter. The data collection was performed on the BL14.3 Beamline of the MX-facility at Helmholtz Zentrum Berlin für Materialien und Energie, equipped with 1-cirlcle goniometer and Mar MX-225 CCD detector (Rayonics, Illinois).[67] The experiment was performed at room temperature (22 °C) using monochromatic synchrotron radiation with λ = 0.89499 Å (E = 13.5 keV). 180 images were collected using φ-scan with

oscillation steps $\Delta\varphi = 0.5°$ and exposition time 10 s/frame. The dataset was processed in automatic regime using XDSAPP 2.0 software.[68] The crystal structure was solved by direct methods and refined with anisotropic ellipsoids for all non-hydrogen atoms by full-matrix least squares on F^2 using SHELX-2016/4 program package.[69] After refinement of the framework, the position of the Cl⁻ anion was determined from the difference Fourier map. The occupancy of the Cl⁻ anion was refined and then fixed in the final refinement cycle. In the final refinement, SWAT instruction was used in order to model the diffused solvent molecules in the pores. CCDC-1838419 contains the supplementary crystallographic data for DUT-67(Zr)_HCl. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The main experimental data are given in table 1.

Table 1. Experimental data for single crystal X-ray diffraction experiment for DUT-67(Zr)_HCl.

	DUT-67(Zr)_HCl
Empirical formula	$C_{24}H_8Cl_{0.86}O_{32}S_4Zr_6$
Formula weight	1514.23
Crystal system, space group	Cubic, $Fm\bar{3}m$
Unit cell dimensions, Å	$a = 38.650(4)$
Volume, Å^3	57736(20)
Z	24
Calculated density, g/cm^3	1.045
μ, mm^{-1}	1.452
T_{min}, T_{max}	0.972, 0.972
θ range, deg	1.149 – 32.48
Limiting indices	$-47 \leq h \leq 39$
	$-48 \leq k \leq 35$
	$-50 \leq l \leq 44$
Reflections collected / unique	54700 / 3520
$R(int)$	0.0995
Data / parameters	3520 / 93
GooF on F^2 [$I>2\sigma(I)$]	1.019
GooF on F^2 (all data)	1.019
$R1$ [$I>2\sigma(I)$]	0.0872
$wR2$ [$I>2\sigma(I)$]	0.3450
$R1$ (all data)	0.1154

wR2 (all data)	0.4062
Largest diff. peak / hole, $e\text{Å}^{-3}$	2.451 / -3.041

Results and discussion

To obtain the DUT-67 materials containing Cl^- or SO_4^{2-} counter-ions, a post-synthetic exchange route was chosen. Recently, solvent assisted linker incorporation (SALI) has been introduced as promising strategy to functionalize $[Zr_6(\mu_3\text{-OH})_8(OH)_8]^{8+}$ node of NU-1000, also an eight connected framework, where the terminal -OH groups were replaced by carboxylic acids containing functional group.[70,71]

This route involves a treatment of the parent DUT-67 MOF, containing formate as monodentate ligand (modulator), with hydrochloric or sulfuric acid, respectively. As a result, highly crystalline materials could be obtained, where the modulator molecules, as well as a part of the DMF molecules are replaced by Cl^- or SO_4^{2-} and the solvent of choice. In such a way, the comparability of the samples could be guaranteed, and the influence of synthetic conditions could be minimized. The samples obtained in the post-synthetic treatment are referred to as DUT-67_HCl (sample treated with HCl) and DUT-67_H_2SO_4 (sample treated with H_2SO_4).
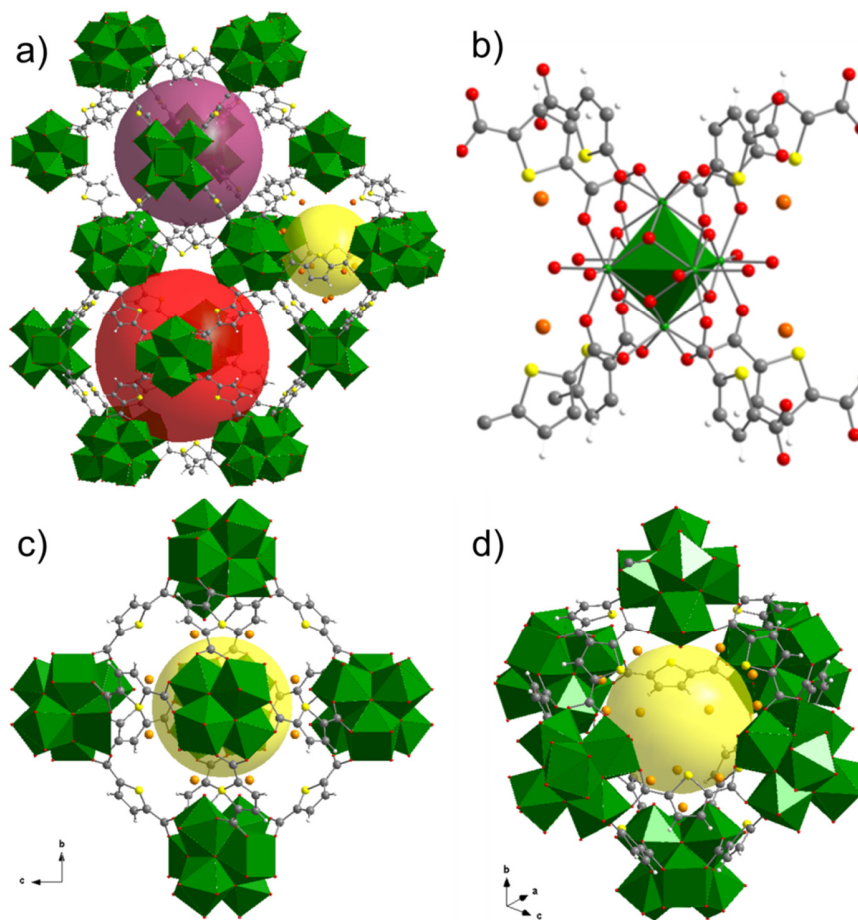
Figure 1. a) Crystal structure of DUT-67_HCOOH.[66] The colored spheres represent three different pores: small octahedral micropore in yellow, small cuboctahedral pore – in violet, big cuboctahedral pore – in red. b) Local cluster environment of DUT-67 (Zr)_HCl. Zr atoms are shown in green, carbon in grey, oxygen in red, sulfur in yellow, chloride in orange. c – d) Positions of chlorine anions in the small octahedral pore (shown in yellow in Fig. 1a)

In general the degree of anion exchange depends on the crystal size, time of treatment, and concentration of the acidic solution. Since the crystal size of DUT-67, which was used for the modulator exchange, was small (~ 1.2 µm, Fig. S19), low concentrated acid solution (2 wt.%) and short time (four hours only) were sufficient to remove the majority of the modulator molecules. A kinetic study, where the modulator/linker ratio was monitored *via* ^{1}H-NMR, shows that more than half of the formates are removed by hydrochloric acid after 10 minutes (Section S2 ESI, Fig. S7).

In case of treatment of the parent material with 5 wt.% H_2SO_4 solution for 24 hours, the crystallites were completely dissolved. If the material is treated with 2.wt% H_2SO_4 solution, the MOF retains the crystallinity, but shows already after four hours of treatment missing linker defects, according to TG analysis (Figures S3, S4).

To get more insights into anion exchange process, time dependent PXRD measurements (Figure 2a, Figure S8a, ESI) were performed during the HCl treatment. The measurements show that after a short time of 10 - 30 min the crystallinity decreases and the reflections are broadened. However, after two hours of treatment, the reflections become well-defined and a highly crystalline material is formed after four hours. Furthermore, a sample of DUT-67 with poor quality and very broad reflections show clearly defined and sharp reflections after the acidic treatment with HCl (Figure 2b, Figure S8b, ESI), which indicates a partial recrystallization- and healing process. Thus, extended reaction time (up to 24 h) of HCl treatment leads to a healing of the crystals, resulting in a material with high crystallinity and porosity (Figure S10, Table S2, ESI). The acidic treatment influences not only the crystallinity and porosity, but also water vapour adsorption behavior (Figure 3, Figure S12, ESI). The adsorption isotherm of pristine DUT-67 contains three steps, representing the filling of the three different pore types: the small octahedral pore (yellow sphere in Figure 1a), the cuboctahedral pore with open metal sites (red sphere in Figure 1a) and the cuboctahedral pore without open metal sites (purple sphere in Figure 1a).[63]The water adsorption isotherms of DUT-67_HCl and DUT-67_H_2SO_4 have much steeper slope in the low p/p_0 region, indicating a more hydrophilic character of the treated samples in comparison to the pristine material (Figure 3).
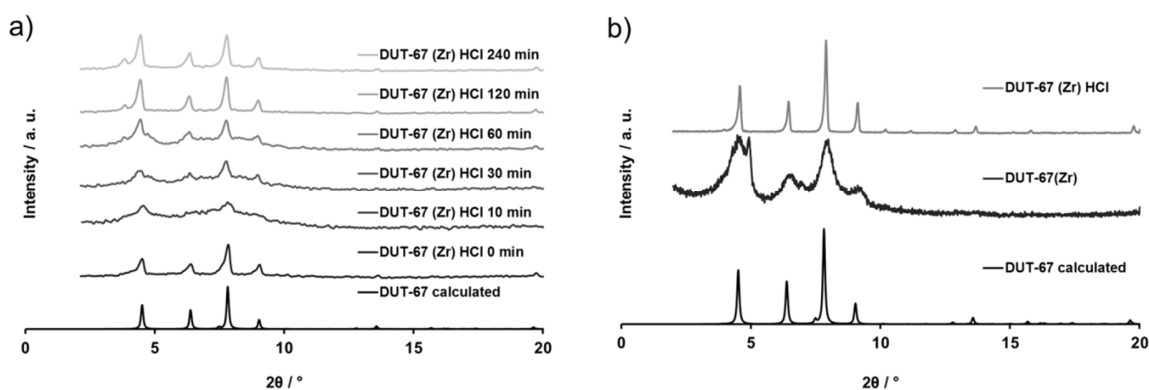
Figure 2. a) PXRD patterns of DUT-67(Zr), which was treated with a 2 wt.% solution of HCl for different times. b) PXRD patterns of as synthesized DUT-67(Zr) sample of pure crystallinity (dark grey) and after a treatment with a 2 wt.% solution of HCl for 24 hours (light grey).

This higher hydrophilicity of the acid treated samples with respect to the parent material is very relevant for the resulting catalytic properties, as we will discuss later.

In addition, the stability of the treated MOFs against water removal is increased. While total pore volume of pristine DUT-67(Zr) decreases for 37% after water removal, DUT-67(Zr)_HCl shows a porosity loss of 20% and DUT-67(Zr)_H$_2$SO$_4$ of 7% only (Table 2, Figure S11, ESI). The same trend is observed for the Hf based DUT-67. Therefore we conclude that exchange of modulator molecules by Cl$^-$ or SO$_4^{2-}$ does increase the hydrolytic stability/robustness of investigated MOFs. However, the effect on thermal stability is more complex (Figure S9, ESI). DUT-67_HCOOH preserves its crystallinity up to 275 °C. DUT-67_HCl decomposes at 200 °C, which is the temperature region where Cl$^-$ starts to be released from the metal cluster, according to TG/MS analysis (Figure S2, S5, ESI). DUT-67_H$_2$SO$_4$ seems to be stable at even 300 °C.

To get a deeper look into the chemical nature of the DUT-67 cluster, DUT-67_HCOOH and DUT-67_HCl were analyzed by the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Two sharp peaks at 3670 cm^{-1} and 730 cm^{-1} appear in the spectrum of DUT-67_HCl, which can by assigned to the free -OH stretching and -OH bending vibrations, respectively, while no signals relating to such terminal -OH groups were observed in DUT-67_HCOOH (Figure S15, ESI). It points on complete removal of modulator molecules as well as DMF molecules from the cluster to form open zirconium cluster coordinated to terminal hydroxyl groups.
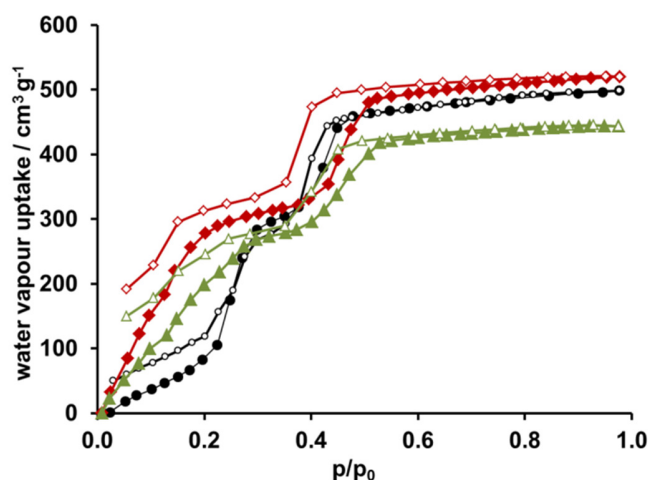
Figure 3. Water adsorption isotherms of DUT-67(Zr) (black circles) and DUT-67(Zr)_HCl (red diamonds) and DUT-67(Zr)_H$_2$SO$_4$ (green triangles) at 298 K.

A single crystal of DUT-67(Zr)_HCl was subjected to the single crystal X-ray diffraction analysis with the purpose to localize the electron rich Cl$^-$ anion in the crystal structure. Indeed, after refinement of the structure of the framework, Cl$^-$ atoms could be localized with the partial occupancy of 10.7%. The chlorine atoms are located on a mirror plane *m*, which corresponds to the 96*k* Wyckoff position in the unit cell. All these positions are located in the smallest and hydrophilic octahedral pore of DUT-67(Zr). The chloride anions are localized next to the metal node of the MOF and separated from the μ$_3$-oxygen atoms O6 by a distance of 3.353 Å. (Figure 1b, Figure S20, ESI). Such interatomic distance is characteristic for the weak OH…Cl interaction, which is probably the main reason for the defined positions of the Cl$^-$ in the crystal structure. As a consequence, the Zr cluster is less shielded by anions in comparison to pristine DUT-67 and are more accessible for substrate molecules. In contrast, in Zr-based MOFs containing sulphate anions, according to Jiang et al.[62], the SO$_4^{2-}$ are located at the corners and/or the edges of the octahedral Zr cluster (Figure S20).

To get an insight into the acid strengths of the materials obtained after acidic treatment, the Hammett indicator method[72,73] was applied (Table S3, ESI). The Hammett acidity H$_0$ allows a qualitative statement about the ability of a material to convert a neutral base to its conjugated acid (Brønsted acidity). If an adsorbed indicator changes the colour to its acidic form, it means that the acid strength of the material is equal or lower than the pK$_a$ value of the indicator. For the UiO-66

and UiO-67 materials, as well as the (Zr and Hf based) pristine DUT-67, the H_0 acid strength ranges between $+6.8 > H_0 > +3.3$. In contrast, the DUT-67 materials, which were treated with sulphuric and hydrochloric acid, increase their acid strength to $+1.5 > H_0 > -3$ (Table S4, ESI).

Table 2. Textural properties of pristine- and acid treated DUT-67.

	Surface area $/m^2\,g^{-1}$ experimental	$tPV_{N2}/$ $cm^3\,g^{-1}$ experimental	$tPV_{N2}/$ $cm^3\,g^{-1}$ after water desorption	$tPV_{H2O}/$ $cm^3\,g^{-1}$ experimental	Porosity loss/ %
DUT-67(Zr)	1110	0.49	0.31	0.40	37
DUT-67(Zr)_HCl	1013	0.46	0.37	0.42	20
DUT-67(Zr)_H_2SO_4	1153	0.48	0.45	0.37	7
DUT-67(Hf)	763	0.33	0.29	0.30	12
DUT-67(Hf)_HCl	791	0.33	0.31	0.28	6
DUT-67(Hf)_H_2SO_4	798	0.33	0.29	0.28	12

tPV_{N2} - pore volume derived from nitrogen adsorption isotherm at 77 K; tPV_{H2O} - pore volume derived from water vapor adsorption isotherm at 298 K.

In order to evaluate the catalytic properties of Zr- and Hf-containing DUT-67 compounds and to investigate the effect of the post-synthetic anion exchange treatments, we decided to use the esterification of levulinic acid with ethanol as a test reaction. We find this test reaction particularly interesting, since it has been recently shown that it can be catalyzed by UiO materials, proving that catalytic sites are accessible to reactant molecules.[74] Given the high connectivity of the Zr_6 clusters in UiO-66 and UiO-67 and the closed coordination sphere of Zr ions, the ideal structures lack the available coordination vacancies, so that open metal sites can only be created at missing linker defects. In contrast, a clear advantage of DUT-67 compounds over UiO-66 is that the lower connectivity of their clusters provides (once the formate modulators are removed) suitable coordinatively unsaturated Zr^{4+} metal centres that can act as the active sites for the esterification

reaction, thus avoiding the need to create lattice defects to display catalytic properties. In addition, coordination of H_2O molecules to coordinatively unsaturated Zr-MOFs also increases the concentration of Brønsted sites provided by hydroxyl groups coordinated to the Zr atoms, as it has been recently demonstrated by a combined experimental and first principles calculations study.[75] In this sense, an increase of the hydrophilic character of the MOF (as a consequence of the treatment with strong mineral acids) is then expected to provide an increase of the Brønsted-induced acidity of the compound. The treatment of DUT-67_COOH with HCl or H_2SO_4 leads to different local coordination environment of the cluster (Fig. S20), which have also to be reflected in different catalytic activity, as we show herein.

For catalytic experiments, batches of pristine DUT-67_HCOOH and acid-treated DUT-67_HCl and DUT-67_H_2SO_4 with similar porosity were chosen. The total pore volumes for DUT-67(Zr) and its acid treated analogues range between 0.46 cm^3 g^{-1} and 0.48 cm^3 g^{-1} and for DUT-67(Hf) between 0.32 cm^3 g^{-1} and 0.33 cm^3 g^{-1} (Table 2).

Table 3 and Figure 4 summarize the results obtained for the esterification of levulinic acid with ethanol using either pristine or acid treated DUT-67 materials as catalysts. For comparison, the results obtained with a UiO-66(Zr) sample[74] containing around 12% of missing linker defects were also included. As it can be clearly observed, the catalytic activity of both as-prepared Zr and Hf based DUT-67_HCOOH MOFs is much lower than that of the reference UiO-66 compound (compare entries 2, 3 and 6 in Table 3). In terms of turnover frequencies (*TOF*), the calculated values for Zr and Hf containing DUT-67 are 6 and 2 h^{-1}, respectively, as compared to 22 h^{-1} obtained for UiO-66(Zr). The lower activity of the as-prepared DUT-67 materials can be attributed to the blocking of the active sites by the formate and DMF molecules, which are still coordinated to the metal sites, thus hampering the adsorption and activation of the reaction substrates. On the other hand, UiO-66 contains a relatively high concentration of missing linkers (*ca.* 12%), and hence also a significant amount of open metal sites, which provides the necessary active centers to carry out the reaction efficiently.

The situation is completely different for the acid treated DUT-67 samples. As we have commented above, acid treatment of the MOFs produces the displacement of both formate and DMF molecules formerly coordinated to the metal ions in the as-prepared material, by the corresponding anions. It translates into a marked increase of their catalytic activity (as compared with the corresponding

as-prepared compounds), largely surpassing that of the reference UiO-66 compound (see entries 4, 5, 7 and 8 in Table 3). The corresponding *TOF*s of the acid-treated DUT-67 compounds are between three and five times higher than the reference UiO-66. In general, Hf materials are found to be less active than the Zr analogues, while the compounds treated with HCl are only slightly more active than the corresponding H_2SO_4 treated materials. The explanation for such minor deviation in the catalytic activity can be attributed to the pivotal role of Brønsted acid sites, since the shielding effect of SO_4^{2-} anions is higher with respect to Cl^- also in conjunction with estimated Hammett acidity.

Table 3. Esterification of levulinic acid with ethanol over pristine and acid treated DUT-67 compounds. Results obtained in a blank experiment and over UiO-66(Zr) (*ca*. 12% missing linker defects) are also included for comparison.[a]

	Catalyst	Time	EL yield (mol%)[b]	*TOF* $(h^{-1})^c$
1	Blank	2 h	1.5	-
		20 h	9.7	
2	UiO-66(Zr)	2 h	54	22
		20 h	99	
3	DUT-67(Zr)_HCOOH	2 h	14	6
		20 h	47	
4	DUT-67(Zr)_HCl	15 min	44	110
		2 h	84	
5	DUT-67(Zr)_H_2SO_4	15 min	34	85
		2 h	78	
6	DUT-67(Hf)_HCOOH	2 h	6.2	2
		20 h	21.6	
7	DUT-67(Hf)_HCl	15 min	33	100
		2 h	77	
8	DUT-67(Hf)_H_2SO_4	15 min	28	72
		2 h	72	

[a] Reaction conditions: Levulinic acid (116 mg, 1 mmol), ethanol (0.9 mL, 15 mmol), catalyst (1.8 mmol.% metal with respect to levulinic acid), 80°C. [b] Determined by GC. Ethyl levulinate was the only product detected. [c] Turnover frequencies (*TOF*, in h^{-1}), calculated as moles of levulinic acid converted per mole of metal and per unit time at short reaction time (at conversion levels below 20 mol%).

Note also that the larger availability of open metal sites in the acid-treated DUT-67 materials, with respect to the pristine material, translates into a stronger coordination of water molecules (as evidenced from the water adsorption isotherms shown in Figs. 3 and S12), which in turn will increase the Brønsted induced acidity of the acid treated materials, and thus, the observed catalytic activity. All materials were found to remain highly crystalline after the reaction, as confirmed by XRD of the used solids, while leaching of Zr (or Hf) from the solid to the reaction medium was ruled out according to ICP-OES analysis of the liquid filtrate. Accordingly, hot filtration experiments at partial conversion showed in all cases that the reactions do not proceed any further when the solid catalysts are removed from the reaction medium, thus evidencing the heterogeneity of the reaction.
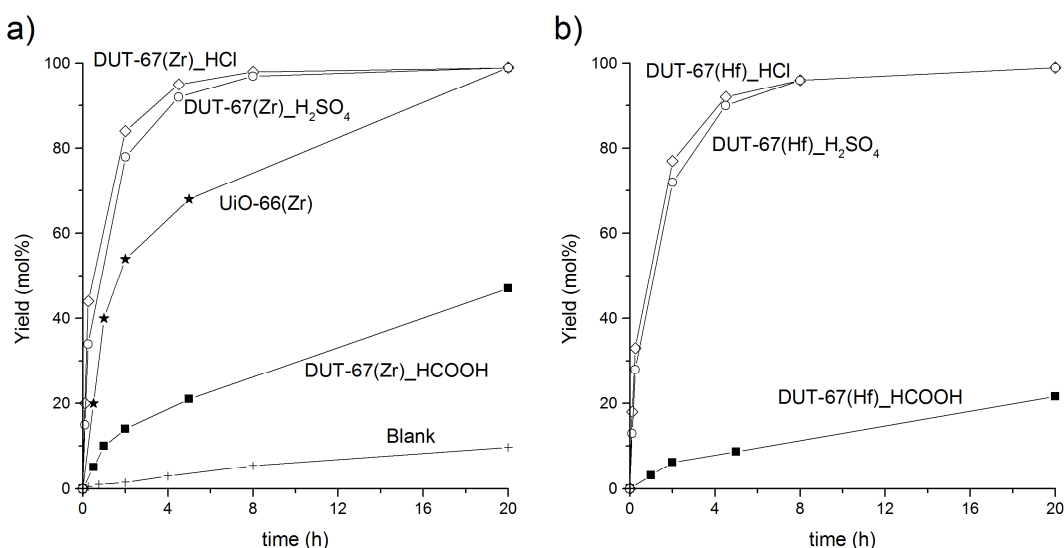

Figure 4. Yield of ethyl levulinate obtained over Zr (part *a*) and Hf (part *b*) based DUT-67 compounds: pristine compounds (-■-); HCl-treated samples (-◊-); and H_2SO_4-treated samples (-○-). Results obtained over an UiO-66(Zr) compound with ca. 12% missing linkers (-*-) and in a blank experiment without catalyst (+) are also included for comparison.

For reusability experiments, the solid catalysts were recovered by filtration, washed with ethanol and dried at room temperature overnight. In all cases, it was found that strong deactivation of the acid-treated DUT-67 samples occurs after the first catalytic cycle (see Section 6 of ESI). However, starting from the third catalytic run, the progressive deactivation of the catalyst is much less

pronounced, as shown in Figure 5 for the DUT-67(Zr)_HCl compound (the behavior of all the other materials was similar). When the spent catalyst recovered after 6 consecutive reuses was washed with H_2O instead of ethanol, it partially recovered its activity, which evidences the relevant contribution to the observed catalytic activity of the Brønsted-induced acidity upon water coordination on the Zr^{4+} open metal sites. Meanwhile washing with an ethanolic solution of 2 wt.% HCl produced a complete recovery of the catalytic activity to the same level of the fresh catalyst.
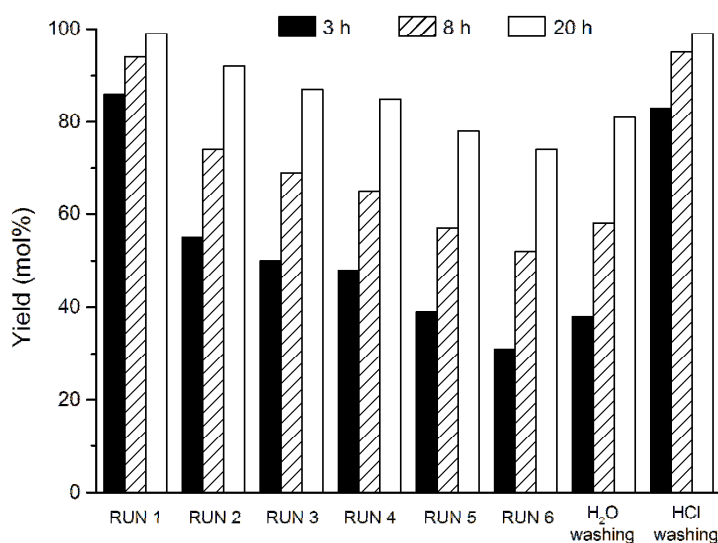

Figure 5. Yield of ethyl levulinate obtained (after 3 h, 8 h and 20 h of reaction) in consecutive recycling experiments of DUT-67(Zr)_HCl. Between two consecutive runs, the solid catalyst was washed with ethanol (runs 1 to 6), or with either H_2O or a 2wt% ethanolic solution of HCl, and dried at room temperature overnight.

Therefore, this (reversible) deactivation of the catalyst can be attributed to the regeneration of Brønsted sites by acidic treatment, as well as desorption and washing of eventually adsorbed products on the catalyst surface. Meanwhile, according to the XRD analysis, the crystallinity of the solid was maintained throughout the whole reusability tests, which evidences the high stability of the MOFs under the selected reaction conditions.

Summary and conclusions

Due to the labile character of ligands in Zr-based MOFs, promoting ligand exchange, a treatment of DUT-67 with an ethanol solution, containing small amount of HCl shows a healing effect. This recrystallization process results in improved crystallinity and porosity. An acidic treatment with HCl or H_2SO_4 changes furthermore the coordination environment of the metal cluster, insofar as modulator molecules are removed from the framework and corresponding anions of the inorganic acids are incorporated for charge balance. Thereby, relevant properties of the MOF are tuned: the hydrophilicity as well as the acid strength is increased. These modifications have a huge impact on the catalytic activity. While pristine DUT-67 has relatively small TOFs in the esterification of levulinic acid with ethanol (6 h^{-1} for Zr based – and 2 h^{-1} for Hf based DUT-67), DUT-67_HCl shows a ~18-fold increase of TOFs (Zr based) and even a 50-fold increase for the Hf based MOF. The sulphate bearing DUT-67 is slightly less active in comparison to DUT-67_HCl, likely due to steric factors. Recycling tests showed some decrease in the catalytic activity, but the activity could be completely regained by a subsequent washing procedure, involving a diluted HCl solution. The full recovery illustrates the importance of absence of molecules, like modulators or other metal coordinating molecules, which block catalytic active centers.

Acknowledgments

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