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Water-based Synthesis of Zr₆-based Metal Organic Framework Nanocrystals with Sulfonate Functions: Structural Features and Application to Fructose Dehydration

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1 Abstract

A series of zirconium-based Metal-Organic Framework (MOF) nanocrystals (95-211 nm) 2 3 displaying sulfonate functions (UiO-66-SO₃H) was prepared in N,N-dimethylformamide 4 (DMF) - the conventional solvent - and water, and their physicochemical properties were 5 thoroughly investigated. In particular, XRD results suggest that upon replacing DMF with 6 water, the resulting MOF crystal structure presents a highly defective structure belonging 7 to the space group Im-3 instead of the typical Fm-3m. The acid catalysts were applied to 8 the fructose dehydration into 5-hydroxymethylfurfural (5-HMF). Complete conversion of 9 fructose over UiO-66-SO₃H prepared in water was reached after only 30 minutes at 100 10 °C, in line with its stronger Brønsted acidity. In comparison, its counterpart prepared in DMF showed only 30 % fructose conversion. Moreover, intrinsic catalytic effect at 80 °C 11 was only observed with the water-based UiO-66-SO₃H. Without reactivation of the 12 catalyst, recycling tests demonstrated the preservation of its structural integrity upon 9 13 consecutive cycles, while a gradual loss of the catalyst activity was attributed to the 14 15 humins adsorption on the MOFs.

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18 Keywords: Metal-organic frameworks, Zr₆ clusters, sulfonate groups, green synthesis,
19 fructose dehydration

1

1. Introduction

2 The studies on conversion of biomass into fine chemicals and fuels has 3 significantly increased over the past years highlighting biomass as a sustainable feedstock 4 for the production of a variety of valuable chemicals [1-3]. Lignocellulosic biomass is of 5 particular interest, as it does not compete with food production. Generally, lignocellulosic biomass consists of three major polymeric components: lignin (~25 %), cellulose (~45 6 7 %) and hemicellulose (~30%) [4]. Upon acidic pretreatment, cellulose and hemicellulose are depolymerized into hexoses and pentoses, respectively [5,6]. This step is crucial as it 8 9 allows to obtain convertible sugar monomers from carbohydrate polymers in a cost-10 effective way, however technologically challenging at large scale. Other pretreatment 11 technologies include physical (mechanical, ultrasound, microwave), chemical (acid, 12 alkaline), and biological (microbes, enzymes) methods [7]. Thereafter, many reactions 13 may be performed to convert the sugar monomers into more valuable products, such as hydrogenation, isomerization, and deoxygenation [8]. Specifically, fructose is the product 14 15 of glucose isomerization which is oftentimes catalyzed by enzymes (Figure 1) [9].

One of these particularly interesting reactions is the dehydration of fructose to 5-HMF which is amongst the top-10 platform molecules, building blocks that can be further transformed into a variety of valuable products. For example, further oxidation of 5-HMF leads to the formation of 2,5-furandicarboxylic acid (2,5-FDCA), which is a potential green alternative to terephthalic acid for the production of polyesters, notably polyethylene terephthalate (PET) [10].

Dehydration of fructose to 5-HMF (Figure 1) is a one-step reaction which is usually performed in liquid phase, using various solvents such as water [11], organics [12], biphasic systems [13] and ionic liquids [14]. In addition, different activation approaches have been applied such as conventional [15] and microwave [16] heating.

Generally, dehydration of fructose itself is catalyzed by Brønsted acids. For instance, 1 2 dehydration of fructose using a HCl/DMSO (dimethyl sulfoxide) mixture at 90 °C 3 reached a conversion of 97 % and a 5-HMF yield of 69 % in 2 h [17]. Similar results were obtained when formic acid was used as the catalyst in a water/n-butanol mixture at 170 4 5 °C, with 98 % conversion and 5-HMF yield of 69 % [18]. Currently, the industrial process 6 is based on hydrothermal carbonization (HTC) of sugarcane biomass and gives 5-HMF 7 with a purity as high as 99.9 % for a rough capacity production of 20 tons per year [19]. 8 Albeit both high conversion and yield could be achieved following homogeneous 9 catalytic processes, reactor corrosion and loss of the soluble catalyst from the mixture is 10 particularly problematic.



Figure 1. General process pathway towards production of 5-HMF from lignocellulosicbiomass.

11

Apart from mineral and organic acids, a wide variety of solid acid catalysts have been tested in fructose dehydration. Namely, zeolites [20], ion-exchange resins [21] or functionalized porous materials [22] have demonstrated good activity in fructose dehydration. For instance, fructose conversion reached 72 % with 55 % 5-HMF yield over H-beta (Si/Al = 25) nanozeolite after 2 h in DMSO at 120 °C [23]. Likewise, sulfonic acid-grafted mesoporous silica, SBA-15-SO₃H, showed 99 % conversion and 81 % 5-

HMF yield after 1 h at 120 °C in ionic liquid [BMIM]Cl [24]. Complete fructose 1 2 conversion at 120 °C as well as 100 % 5-HMF yield were obtained in DMSO after 2 h 3 over Amberlyst-15 under continuous evacuation of the released water resulting in an increase of the product yield [25]. Additionally, remarkable 100 % fructose conversion 4 and 93 % 5-HMF yield were obtained also in DMSO after 1 h over Amberlyst-70 at 140 5 °C [26]. It should be noted that such high temperatures (≥ 120 °C) hinder the cost-6 7 efficiency of the overall process. The development of alternative catalysts, allowing to 8 work at mild temperatures, would thus be highly attractive.

9 Over the past ten years, MOFs have been extensively investigated. Their structure 10 is comprised of metal nodes (ions or clusters) and organic linkers (for example, di- and 11 tricarboxylic acids). Together they form highly crystalline porous solids. Owing to their unique combination of large surface area, controllable pore size as well as high 12 physicochemical properties tunability, they have been used in various applications such 13 as heterogeneous catalysis [27], waste-water purification [28], toxic gas removal [29] and 14 gas storage [30], sometimes even unveiling performances unreachable by conventional 15 porous solids [31]. 16

17 One of the most famous and well-studied MOFs is the UiO-66 (Universitetet i Oslo) compound. This MOF is composed of $Zr_6O_4(OH)_4^{12+}$ clusters connected by 18 terephthalate linkers to form a continuous 3D structure with a cubic symmetry of the unit 19 cell (*Fm-3m* space group), an approximate surface area of ~1000-1200 m²·g⁻¹ and pores 20 21 size below 2 nm [32]. Due to the phenomenon known as "missing linkers", the classical UiO-66 exhibits Lewis acidity thanks to the Coordinatively Unsaturated Sites (CUS) on 22 23 Zr-oxoclusters, which can be active in sugar isomerization. Thus, upon isomerization of glucose over UiO-66, fructose yield reached ~35 % at ~50 % glucose conversion at 90 24 °C in 1-PrOH [33]. However, in order to make the classical UiO-66 highly active in sugar 25

dehydration, Brønsted acid sites and especially sulfonic acid functions should be inserted
into the framework of the MOF. Indeed, UiO-66-SO₃H analogues have shown to improve
the dehydration activity compared to the non-functionalized UiO-66. Thus, one-pot
glucose conversion *via* dehydration of fructose into 5-HMF at 140 °C resulted in an
increased 5-HMF yield from 3 % to 8 % upon increasing the content of -SO₃H functions
up to 20 wt.% [34].

Similarly, direct fructose dehydration into 5-HMF over MOFs with sulfonic acid
functions leads to a considerable increase in conversion and product yield. Thus, the postsynthetic functionalization of MIL-101(Cr) led to complete fructose conversion with 90
% 5-HMF yield in 1 h at 120 °C, whereas the non-functionalized MOF exhibited a
fructose conversion of 45 % and 5-HMF yield of 24 % [35].

Currently, one of the main issues for the use of UiO-66 and its functionalized 12 derivatives at industrial scale is that their synthesis often uses DMF, a well-known 13 hazardous and toxic solvent. It is classified as toxic to reproduction, acute toxicant 14 (inhalation and dermal route) and as an eye irritant in accordance with EU Regulation 15 (EC) No 1272/2008. Moreover, DMF could be responsible for severe liver damages upon 16 17 exposure, provoking hepatitis and cancer [36]. Therefore, there is a need to establish strict 18 regulation rules for the use of DMF. Recently, the European Commission adopted a regulation amending Annex XVII of REACH (Registration, Evaluation, Authorisation 19 and Restriction of Chemicals) to restrict the solvent on the EU market starting from 20 21 December 2023. DMF remains required for the synthesis of classical UiO-66 as its ligand, terephthalic acid, is insoluble in most conventional solvents. This is the reason why 22 23 functionalized UiO-66 analogues are also frequently made in DMF [37–39]. Therefore, the replacement of DMF is seen as an essential strategy for MOFs synthesis. To date, a 24 25 few papers have reported sustainable methods for the preparation of MOFs [40,41].

Particularly, green and scalable syntheses of UiO-66-based functionalized MOFs have 1 2 been extensively developed within the past few years due to decent solubilities of the 3 functionalized terephthalate linkers in water. Interestingly, the procedures for tuning the chemical properties of conventional porous solids such as zeolites, carbons or silicas is 4 more complex as compared to the MOFs, especially in green conditions. Therefore, the 5 list of UiO-66-X prepared in water includes the following nominations: UiO-66-COOH 6 UiO-66-(COOH)₂ [43,45–47], UiO-66-(COOH)₄ [47], UiO-66-NH₂ 7 [42-44],8 [43,44,46,47], UiO-66-NO₂ [48], UiO-66-F₄ [45–47], UiO-66-(OH)₂ [43,47], and UiO-9 66-SO₃H [49].

10 As evident from Table S1, the variety of functionalized MOFs derived from UiO-11 66 can be as large as the number of existing terephthalate-derived linkers. Of note, varying the Zr-source also leads to porous MOFs with decent available surface areas. 12 13 Therefore, the present work is exploring water-based synthesis of UiO-66-SO₃H MOF with emphasis on synthesis condition optimization and the resulting physicochemical 14 properties, as well as its performance in fructose dehydration to 5-HMF with respect to 15 UiO-66-SO₃H prepared in DMF. UiO-66 was chosen as the target MOF due to its good 16 17 textural properties, thermal and chemical stabilities [50] as well as its chemical properties 18 tunability [37,51]. Direct recyclability of the water-based UiO-66-SO₃H over subsequent 19 runs, which simulates to some extent its use in a continuous process using batch conditions, was also investigated. 20

- 21 **2. Experimental**
- 22 2.1 Materials

Zirconium chloride (99.5 %, Alfa Aesar), zirconium sulfate tetrahydrate (98 %,
Alfa Aesar), terephthalic acid (99 %, Acros Organics), monosodium 2-sulfoterephthalate
(98 %, TCI Chemicals), D-fructose (99 %, Acros Organics), N,N-dimethylformamide

(pure, Carlo Erba Reagents), dimethyl sulfoxide (99.7 %, Fisher BioReagents), acetic acid
 (100 %, VWR), ethanol (96 %, VWR), and 5-(hydroxymethyl)furfural (98 %, Acros
 Organics) were used as-received.

4 2.2 Catalysts preparation

5 UiO-66 was synthesized following the methodology previously described by Foo et al. [37]. Namely, 0.32 g of ZrCl₄ and 0.22 g of terephthalic acid (molar ratio of 1:1) 6 7 were dissolved in 100 mL of DMF. Upon dissolution, 3 mL of acetic acid were added and 8 thereafter the entire solution was placed in the PTFE (polytetrafluoroethylene) liner of a 9 stainless-steel autoclave and heated at 120 °C for 24 h. After crystallization, a white solid 10 product was recovered by centrifugation and washed in fresh DMF at 50 °C to dissolve 11 unreacted species. This was followed by 3 consecutive washing steps in ethanol at 50 °C. Eventually, the product was recovered and dried overnight at 100 °C. 12

The preparation of UiO-66-SO₃H-D was done similarly, by dissolving 0.31 g of ZrCl₄ and 0.35 g of monosodium 2-sulfoterephthalate (molar ratio of 1:1) and adding acetic acid in 100 mL of DMF. All other steps are identical as in the case of UiO-66. For comparison, a material with a molar ratio of 1:2 was also prepared.

For UiO-66-SO₃H-W preparation, 1 g of Zr(SO₄)₂·4H₂O and 1.44 g of monosodium 2-sulfoterephthalate (molar ratio of 1:2) were dissolved in 100 mL of water. The resulting solution was heated up to 100 °C under reflux, as a simpler alternative to solvothermal conditions. The resulting white solid was recovered and washed 3 times with fresh H₂O as well as with ethanol at 50 °C overnight. Upon washing, the product was dried at 100 °C overnight. For comparison, materials with a molar ratio of 1:1 and with either ZrCl₄ or Zr(SO₄)₂·4H₂O were also prepared.

24 2.3 Catalysts characterization

Powder X-Ray Diffraction (XRD) patterns were recorded on a D8 Advance
 instrument from Bruker, equipped with a CuK_α X-ray source (λ = 1.54184 Å), using the
 following parameters: 2θ range between 5-40 °, scan rate of 0.02 °/step, and acquisition
 time of 1 s/step. The simulated pattern of UiO-66-SO₃H was plotted using its CIF file
 provided by Taylor *et al.* [49].

6 Textural properties were measured by N₂ physisorption experiments performed at 7 77 K using a Micromeritics Tristar II instrument. Before analysis, a known mass (~ 50 8 mg) of solid was treated at 120 °C under vacuum for 15 h. Specific surface area (S_{BET}) 9 was calculated using the B.E.T. method, on the linear part of the B.E.T. plot ($p/p_0 = 0.1$ -10 0.3). Pore volume was calculated using the adsorption branch of the isotherms at a p/p_0 11 value of 0.99. Pore size distribution from 1.0 nm was given by the non-local density 12 functional theory (NLDFT) model.

Scanning electron micrographs were registered on a JEOL JSM 6700F microscope
in the range of 5-10 kV. Before observation under microscope, the samples were covered
with a thin layer of Cr (150 Å).

Infrared spectra (IR) were measured on a Perkin–Elmer "Spectrum Two"
spectrometer equipped with a diamond and operating in the attenuated total reflectance
(ATR) mode between 4000 and 400 cm⁻¹.

Raman spectra were recorded on an XPlora Plus from Horiba Scientific microspectrometer equipped with a 50X focal length objective. The acquisition of spectra was
performed using a laser excitation wavelength of 532 nm and a 50 % filter to avoid
possible sample degradation under the laser beam.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a Kratos
 Axis Ultra DLD instrument equipped with a monochromatized AlK_α X-ray source
 powered at 225 W (15 mA, 15 kV). The base pressure in the analysis chamber was lower

than 5.10⁻⁹ Torr. General survey spectra were recorded at a 160 eV pass energy and Zr 3d,
C 1s, O 1s and S 2p core level spectra were recorded at a 20 eV pass energy. The Kratos
charge compensation system was used during all analysis, and Binding Energy (BE)
scales were adjusted according to the Zr 3d_{5/2} peak placed at 182.8 eV. The relative
surface atomic quantification was obtained after the subtraction of a Shirley type
background on all spectra.

Thermogravimetric analysis (TGA) profiles were obtained with a thermal
analyzer instrument Q600 from TA Instrument within the temperature range 25 – 800 °C
at a heating rate of 5 °C·min⁻¹ in air flow (100 mL·min⁻¹).

10 Chemical composition of the catalysts was determined by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Analyses were performed on a 11 Perkin Elmer Optima 2000 DV instrument to determine the chemical composition of the 12 13 solids based Zr. S and Na. Before on analysis, known a amount of sample was dissolved in a diluted HF-HCl solution, and then heated under 14 microwave until complete dissolution. 15

Acid site density of the catalysts was estimated by acid-base titration method. For this, 0.1 g of solid was immersed into 100 mL of 1M NaNO₃ solution and left overnight under constant stirring. This step was repeated 3 times. After that, the mixture was centrifugated and a 50-mL aliquot was titrated with 0.01 M NaOH solution using phenolphthalein as color indicator [35].

21 2.4. Catalytic tests

Fructose dehydration reaction was performed in a Carousel 12 Plus Reaction Station from Radleys, working at atmospheric pressure, using 1.2 mmol of fructose, 2 mL of DMSO and 20 mg of catalyst. The reaction mixture and the catalyst were stirred at 600 rpm and heated to the desired reaction temperature (80-120 °C) with a reaction time up

to 6 h. At the end of the reaction, the reactors were cooled to room temperature and the 1 products were removed with a syringe, filtered and diluted 10 times using a 5 mM sulfuric 2 3 acid solution. The products were analyzed in high-performance liquid chromatography (HPLC) equipped with UV-vis and refractive index (RID) detectors and a Rezex ROA-4 Organic Acid column using sulfuric acid (5 mM, 0.6 mL·min⁻¹) as a mobile phase. For 5 the recycling experiments, the catalyst was separated by centrifugation and then reused 6 7 directly for the next run with a fresh fructose solution in DMSO. The fructose conversion 8 and 5-HMF yield were defined as:

9 **Conversion** (%) =
$$\frac{\text{mol of Fructose}_i - \text{mol of Fructose}_f}{\text{mol of Fructose}_i}$$
 (1)

10
$$Yield(\%) = \frac{\text{mol of HMF}}{\text{mol of }Fructose_i}$$
 (2)

11 **3. Results and discussion**

12 3.1. Catalyst characterization

13 Figures 2.a and S1 show the XRD patterns of the as-synthesized UiO-66 and the 14 sulfonate-functionalized MOFs prepared in DMF (UiO-66-SO₃H-D) or in water (UiO-66-SO₃H-W). It appears that a ratio of 1:2 was necessary to obtain a highly crystalline 15 16 sulfonic-functionalized MOF in water, while from a ratio of 1:1 the obtained UiO-66 and UiO-66-SO₃H-D were of similar crystallinity. Owing to the difficulty to activate MOFs 17 18 with large amounts of linkers trapped within their porosity, only the ratio of 1:1 will be considered next for the MOFs synthesized in DMF. As expected, the prepared UiO-66 19 exhibits characteristic reflections at approximately 7.4, 8.4 and 25.5 $^{\circ}$ (2 θ) corresponding 20 21 to the (111), (002) and (006) planes, respectively [32]. A similar XRD pattern was 22 obtained for UiO-66-SO₃H-D implying that, using DMF as solvent, the presence of -SO₃H groups does not change the topology of the resulting MOF: a face-centered cubic 23

organization in the unit cell (*Fm-3m* space group, a = 20.7004 Å). Interestingly, the 1 2 pattern of UiO-66-SO₃H-W obtained after 24 h of crystallization time exhibits several 3 additional reflections. Indeed, when synthesized in water, UiO-66-SO₃H adopts a unique topology representing a cubic organization with a doubled unit cell parameter (Im-3, a =4 41.4906 Å) and a lowered crystallographic symmetry [49,52]. This phenomenon is related 5 to a large number of structural defects, with only 8 linkers coordinating the Zr₆ clusters 6 7 instead of 10 to 12 [49]. Then, upon changing the solvent from DMF to water, a UiO-66-8 SO₃H MOF with slight differences in terms of physico-chemical properties was obtained. 9 Especially, due to its defective framework, higher textural properties are expected. Of 10 note, few authors attributed a different name to the resulting MOF structure: NUS-6 [53].



11

Figure 2. XRD patterns of UiO-66, UiO-66-SO₃H-D and UiO-66-SO₃H-W (a) and UiO66-SO₃H-W prepared in water with various synthesis durations (b).

To optimize the preparation of UiO-66-SO₃H-W, crystallization kinetics was studied at 100 °C and the related XRD diffractograms are displayed in Figure 2.b. Semicrystalline solids yielding broadened reflections can be observed from 3 h, and upon 15 h the MOF crystallization process was complete as the obtained solids possessed welldefined reflections in line with the simulated pattern.

Such tendency is in agreement with the results obtained by N₂ porosimetry 1 2 analysis. N₂-sorption isotherms are given in Figure S2 and the related data are provided in Table S2. A successive increase of adsorbed N2 in the micropore region is observed 3 upon crystallization time, hence leading to higher available surface areas and confirming 4 the obtention of better crystallized microporous materials. Of note, a small N2 uptake at 5 high partial pressures (p/p_0) indicates the presence of intercrystalline porosity which is 6 generally observed with small crystals. Owing to its decent yield and SBET, only the UiO-7 8 66-SO₃H-W prepared within 24 h will be considered hereafter.

9 The impact of the linker and the type of solvent over the final textural properties 10 can be deduced from N₂ physisorption isotherms depicted in Figure 3. The type I adsorption/desorption isotherms, with a plateau at low relative pressures ($p/p_0 < 0.2$) for 11 all studied solids, are characteristic of microporous materials. The slight uptake observed 12 13 at high relative pressure $(p/p_0 > 0.9)$ is typical of intercrystalline porosity for nanomaterials. Furthermore, the presence of sulfonic acid functions may be deduced from 14 the significantly lower nitrogen adsorbed at any partial pressure, as the functions occupy 15 an important space within the porosity of the MOF. As seen in Table 1, the non-16 functionalized UiO-66 exhibits the highest specific surface area (1206 $m^2 \cdot g^{-1}$) and 17 micropore volume $(0.47 \text{ cm}^3 \cdot \text{g}^{-1})$ as opposed to the UiO-66-SO₃H materials. The 18 synthesis of UiO-66-SO₃H in DMF leads to a significant decrease of about 60 % in 19 specific surface area (468 m²·g⁻¹) and micropore volume (0.19 cm³·g⁻¹). Of note, Biswas 20 21 et al. also prepared UiO-66-SO₃H in DMF and obtained a specific Langmuir surface area of 769 m²·g⁻¹ and a micropore volume of 0.26 cm³·g⁻¹ [39]. Herein, when DMF is replaced 22 by water, a micropore volume of 0.26 cm³·g⁻¹ is also obtained along with a BET surface 23 area of 639 m²·g⁻¹ (-47 % as compared to the reference UiO-66) after 24 hours of 24 crystallization time. After 72 hours, the resulting BET surface area (630 m²·g⁻¹) remains 25

within the experimental and apparatus errors ($\pm 5 \text{ m}^2 \cdot \text{g}^{-1}$). Regarding the pore size 1 2 distribution, from 1 nm all materials display similar pore widths centered around 1.25 nm 3 and 1.50 nm (Figure S3). UiO-66-based MOFs should also present a pore width centered around 0.6 nm [32], which could not be probed by the apparatus used. Therefore, the use 4 5 of a modulator (acetic acid) or the replacement of DMF by water result in mostly 6 comparable specific surface areas, microporous volumes and pore widths for both 7 sulfonate-functionalized MOFs, but with an expected drop as compared to the original 8 UiO-66 due to the presence of bulky sulfonate moieties.





Figure 3. N₂ physisorption isotherms of the UiO-66-based catalysts.

The Brønsted acidity of both UiO-66-SO₃H was estimated via acid-base titration 11 method. UiO-66-SO₃H-W presents an increased acid sites density as compared to its 12 counterpart prepared in DMF (0.77 mmol \cdot g⁻¹ vs 0.49 mmol \cdot g⁻¹). The higher available 13 surface area of the former does not fully support this increase, as the acid sites density 14 remains 15 % higher when expressed in μ mol·m⁻² (Table 1). This either implies that some 15 acid sites are inaccessible, or that more linker defects are present in UiO-66-SO₃H-D due 16 17 to lower Zr:linker ratio used for its synthesis. Besides, post-modification of UiO-66 into UiO-66-SO₃H in the reference work by Chen et al. [35] led to an acid sites density of 18

1 $0.41 \text{ mmol} \cdot g^{-1}$, underlining that direct synthesis seems a better method to obtain more

2 acidic catalysts.

Catalysts	S _{BET}	V _{total} V _{micro}		Acid sites density ^b		
	$(m^{2} \cdot g^{-1})$	$(\mathbf{cm}^3 \cdot \mathbf{g}^{-1})^a$	(cm ³ ·g ⁻¹)	(mmol·g ⁻¹) (μ mol·m ⁻²)		
UiO-66	1206	0.53	0.47	-	-	
UiO-66-SO ₃ H-D	468 (-61 %)	0.21 (-60 %)	0.19 (-60 %)	0.49	1.05	
UiO-66-SO ₃ H-W	639 (-47 %)	0.27 (-49 %)	0.26 (-45 %)	0.77	1.21	

3 **Table 1.** Textural and acid properties of the as-synthesized MOFs.

4 ^{*a*} Derived from adsorption branch of isotherms at $p/p_0 = 0.99$;

5 b Estimated by acid-base titration.

6 Direct evidence of -SO₃H groups presence on the surface of MOFs is given by FTIR-ATR and Raman spectra shown in Figure 4. Firstly, the bands corresponding to the 7 principal vibrations of the UiO-66 framework are present in all the studied solids. 8 Namely, the IR bands at ~1388 cm⁻¹ and 1587 cm⁻¹ are characteristic of symmetric and 9 asymmetric stretching mode of v(O-C-O) in the terephthalate linker, respectively. While 10 its asymmetric mode is inactive in Raman, the symmetric mode is viewed as the "doublet" 11 band at 1427 cm⁻¹ and 1450 cm⁻¹ in UiO-66 and as an overlapped band in both UiO-66-12 SO₃H-D and UiO-66-SO₃H-W. The small IR band at 1508 cm⁻¹ stem from v(C=C) of the 13 benzene ring which corresponds to the intense band at ~1615 cm^{-1} in the Raman spectra. 14 Moreover, there are IR bands below 1000 cm⁻¹ corresponding to a combination of 15 vibrations: C-H (745 cm⁻¹), µ₃-O (~640 cm⁻¹) stretching [32]. A small shift of the IR and 16 17 Raman bands on UiO-66-SO₃H-D and UiO-66-SO₃H-W spectra towards higher wavenumbers as compared to the classical UiO-66 might be due to the presence of -SO₃H 18 groups. Importantly, both functionalized UiO-66-SO₃H-D and UiO-66-SO₃H-W 19 20 exhibited new IR bands that correspond to S-O vibrations (~620 and 1070 cm^{-1}) and S=O

vibrations (~1170 and 1233 cm⁻¹), which are coherent with the Raman bands at 1025 cm⁻¹ 1 ¹ and 1080 cm⁻¹, respectively [35,54]. Besides, the Raman bands at 1140 and 858 cm⁻¹ 2 correspond to the breathing mode of the linker and C-H in-plane bending, respectively. 3 Importantly, there is also the IR band characteristic of C=O stretching at ~1665 cm⁻¹ in 4 both UiO-66 and UiO-66-SO₃H-D, which allows tracing DMF by its carbonyl group [55]. 5 6 Thus, this reveals the presence of residual DMF in the pores of these MOFs despite a 7 rigorous activation step, especially in the case of UiO-66-SO₃H-D and even after drying 8 under vacuum (Figure S4). This may be due to the presence of bulky sulfonate moieties, 9 reducing the diffusion within the porosity. Of note, the presence of DMF contributes to 10 lower the specific surface area and the estimated amount of acid sites, as compared to the 11 DMF-free UiO-66-SO₃H-W.



Figure. 4 FTIR-ATR (left) and Raman (right) spectra of the synthesized MOFs: a – UiO66, b – UiO-66-SO₃H-D, c – UiO-66-SO₃H-W.

The crystal morphology of all the studied materials was visualized by SEM, and representative images are given in Figure S5. The classical UiO-66 is constituted of wellfaceted, octahedrally-shaped nanocrystals with a narrow particle size distribution around 132 nm. At the same time, the two sulfonated analogues exhibit distorted nanocrystals inhomogeneous in shape and with an average size above that of UiO-66, as reported in

- 1 Table 2. This distortion can be attributed to the presence of -SO₃H groups within the MOF
- 2 frameworks.



Figure 5. XPS spectra of the as-synthesized solids: UiO-66-SO₃H-D survey (a), Zr 3d (b)
and S 2p (c) as well as UiO-66-SO₃H-W survey (d), Zr 3d (e) and S 2p (f).

6 It has been evidenced that UiO-66 MOFs are prone to structural defects estimated 7 from the number of missing linkers. A rough estimation of the latter was made via TGA measurements (Figure S6) using a method described by Shearer et al. [56]. Accordingly, 8 the classical UiO-66 exhibited one missing terephthalate ligand per Zr₆-cluster while the 9 10 two functionalized MOFs surprisingly exhibited approximately 2.3 missing ligands per cluster. These results were further supported by ICP elemental analysis, according to 11 12 which UiO-66-SO₃H-D and UiO-66-SO₃H-W had 1.51 and 1.41 zirconium atoms per sulfur atom, respectively. This, in turn, suggests that UiO-66-SO₃H-D would actually be 13 slightly more defective than UiO-66-SO₃H-W, owing to the large concentration of 14 modulators (acetate from acetic acid and formate from DMF degradation) in the synthesis 15 mixture. Accordingly, the Zr/S surface atomic ratios derived from XPS analysis of UiO-16 66-SO₃H-D and UiO-66-SO₃H-W are 1.60 and 1.46, respectively (Figure 5). This agrees 17

1 well with previous studies [49]. The resulting molecular formula of UiO-66-SO₃H-W is

2 thus $Zr_6O_4(OH)_4[C_6H_3(COO)_2SO_3H]_{4,3}$.

Catalysts	$\mathbf{D}_{\mathbf{c}}(\mathbf{nm})^{a}$	$\mathbf{D}_{\mathbf{p}}(\mathbf{nm})^{\mathbf{b}}$	Zr/S atomic ratio		Missing linkers	
			ICP	XPS ^c	per Zr-cluster ^d	
UiO-66	95	132	-	-	0.9	
UiO-66-SO ₃ H-D	98	183	1.56	1.60	2.3	
UiO-66-SO ₃ H-W	105	211	1.41	1.46	2.3	

3 **Table 2.** Crystallite and particle sizes, and sulfur content of the as-synthesized catalysts.

^a Average crystallite size determined using Scherrer's equation applied to the (111) and
the (002) planes; ^b Average particle size measured by SEM; ^c Only the -SO₃H component
from S 2p spectra was taken into account to calculate the ratio; ^d Determined by TGA.

Examination of UiO-66 S 2p (Figure S7) spectrum reveals that in this material,
which is free of -SO₃H moieties, sulfur traces were found. The spectrum was decomposed
into one doublet peak with a S 2p_{3/2} - S 2p_{1/2} energy splitting of 1.18 eV and a S 2p_{3/2} BE
centered at 166.9 eV. This contribution is attributed to a Cluster-bound sulfur from
impurities.

12 S 2p spectra of both UiO-66-SO₃H-W and UiO-66-SO₃H-D are decomposed into 13 two doublet peaks with a S $2p_{3/2}$ - S $2p_{1/2}$ energy splitting of 1.18 eV. These two 14 contributions have their S $2p_{3/2}$ BE centered at 166.5 eV and 167.9 eV. The low BE 15 contribution is attributed to cluster-bond sulfur (noted "Clus" on the spectra), whereas the 16 doublet peak with high BE (noted "Link" on the spectra) is consistent with sulfonate 17 moieties (-SO₃H groups) adjacent to aromatic rings [57]. This latter contribution was used 18 to calculate the Zr/S atomic ratios.

As higher BE is directly related to higher positive oxidation states, it is reasonable
to hypothesize that the acid strength of the low BE sulfur species is lower. Still, it may

impact the acid titration as it is not selective toward sulfonate moieties. Especially, the
relative proportion of S species bound to Zr₆-clusters seems higher in UiO-66-SO₃H-W
as compared to UiO-66-SO₃H-D, which could be due to the use of zirconium sulfate as a
synthesis precursor. Lastly, supported by the absence of a contribution centered at 1071.5
eV on the survey spectra, no sodium was detected implying the complete *in-situ* -SO₃Na
to -SO₃H ion-exchange during synthesis, responsible for the Brønsted acidity.

7

3.2. Fructose dehydration tests

8 Fructose dehydration to 5-HMF in DMSO at 100 °C was evaluated using UiO-66, 9 UiO-66-SO₃H-D and UiO66-SO₃H-W as solid catalysts. Figure 6 shows the conversion 10 of fructose as a function of reaction time for all the catalysts as well as for the blank test 11 (without catalyst). Indeed, according to the literature both DMSO and Brønsted acid sites are able to convert fructose to 5-HMF at 100 °C [35,58]. Notably, the two catalysts 12 prepared in DMF (UiO-66 and UiO-66-SO₃H-D) exhibited approximately the same 13 conversion profiles as the blank test, indicating that they possess a low activity under 14 these reaction conditions. Instead, UiO-66-SO₃H-W catalyst achieved the complete 15 conversion of fructose (> 98 %) already after 30 minutes confirming its superior activity, 16 17 while it remained around 20 % for UiO-66, 30 % for UiO-66-SO₃H-D catalysts and 45 18 % in DMSO alone.

The presence of residual DMF within the porosity of UiO-66-SO₃H-D, as detected by FTIR spectroscopy, may hinder fructose from reaching the Brønsted acid sites. Especially, DMF was always present on the chromatograms upon analyzing the reaction products when the MOFs prepared in DMF were used as catalysts, while it was absent when using UiO-66-SO₃H-W (Figure S8). An additional blank test was conducted with a mixture of DMSO and DMF (3:1 v:v). As a result, no fructose was converted after 2 h at 100 °C in the presence of DMF, as supported by the colorless reaction solution, while 80

% of fructose was converted in DMSO alone yielding a light-brown colored solution 1 2 characteristic of 5-HMF presence (Figure S9). Studies on binary mixtures showed that 3 there is a complexation behavior of DMSO-DMF mixture via H-bond interactions through S and O atoms on DMSO over a wide range of concentrations [59]. The decreased 4 initial fructose conversion rates over UiO-66 and especially UiO-66-SO₃H-D may hence 5 be attributed to the release of DMF in the mixture. Nevertheless, as it is evident from 6 Figure 6 after 2 h, fructose conversion over UiO-66-SO₃H-D surpasses that of the blank 7 8 test (98 % vs 83 %), and the calculated overall rate constant is higher (Figure S10 and 9 Table S3), highlighting the positive effect of acidic -SO₃H groups on fructose 10 dehydration. In all cases, 5-HMF is identified as the major product, with only traces of an 11 unknown product (Figure S8).



12

Figure 6. Conversion of fructose at 100 °C as a function of reaction time over different
catalysts (UiO-66, UiO-66-SO₃H-D and UiO-66-SO₃H-W) and blank test (without
catalyst).

Although UiO-66-SO₃H-W is the most efficient catalyst of the series for converting fructose into 5-HMF, the suppressive effect of DMF present in the catalysts prevent from discussing the effect of the acid site density. While the objective of this study is to prepare environmentally-friendly catalysts for the production of 5-HMF, it 1 should be stressed that the presence of residual DMF should always be assessed prior to

2 dehydration tests.

3 *3.2.1. Effect of reaction temperature*

The effect of temperature (80-140 °C) on the performance of the catalysts in fructose dehydration was further evaluated over UiO-66-SO₃H-W. Figure 7 compares the fructose conversion and yield of 5-HMF after 30 min of reaction carried out with or without UiO-66-SO₃H-W at different temperatures. Furthermore, the related full kinetic profiles are shown in Figure S11.

9 As expected, the increase of temperature improves the conversion of fructose even 10 when considering only the DMSO solvent (blank tests). At 140 °C, for example, full 11 fructose conversion was observed already after 30 min of reaction in both cases - blank and with the catalyst. Furthermore, the liquids after reaction showed an intense brown 12 13 color, in spite of a similar amount of 5-HMF, approximately 75 % of yield. A significant part of the remaining 25 % are constituted of soluble fructose oligomers and insoluble 14 humins which are undetectable by HPLC. These compounds are formed from both 15 16 fructose and 5-HMF [60].

17 When the reaction temperature is decreased to 80 °C, the solvent does not 18 contribute anymore to fructose conversion (blank test) after 30 min (Figure 7). Interestingly, UiO-66-SO₃H-W retains a decent 48 % conversion and 18 % 5-HMF yield. 19 Moreover, it converts 80 % fructose and yields 50 % 5-HMF after 3 h while the blank test 20 21 still shows no conversion, further proving the catalytic effect of the sulfonic acid groups present in the UiO-66-SO₃H-W catalyst (Figure S11). Finally, after 6 h of reaction at 80 22 23 °C, the maximum fructose conversion was 41 % for blank test and 94 % for UiO-66-SO₃H-W with 5-HMF yields of 14 % and 66 %, respectively. Thus, in order to better 24 25 evaluate a catalyst's performance in fructose dehydration using DMSO as solvent, it is proposed to apply rather mild conditions *i.e.* 80 °C (or less) for a maximum duration of
3 h. These conditions would allow to neglect the effect of DMSO and attribute fructose
conversion as well as 5-HMF yield to the solid acid catalyst only. For higher
temperatures, the 5-HMF yield increased quickly with a maximum reached after 2 h, 30
min and 30 min for reactions performed at 100, 120 and 140 °C, respectively (Figure
S11).





Figure 7. Conversion of fructose and yield of 5-HMF for reactions at different
temperatures (30 min). Blk: Blank test; Catalyst: UiO-66-SO₃H-W.

As evident from Table S4, most of the published results on fructose dehydration over MOFs used temperatures of 100 °C and above, which indubitably favor the impact of the DMSO solvent over the catalytic conversion of fructose. In this work, we showed the possibility to reach complete fructose conversion at lower catalyst loading (215 mg fructose : 20 mg catalyst) and temperatures (> 94 % at 80 °C after 6 h).

1	Interestingly, in the reference work [35], fructose conversion over UiO-66-SO ₃ H
2	reached ~85 % with a 5-HMF yield of ~70 % in 30 min at 120 $^{\circ}$ C as compared to 100 %
3	and 76 % respectively in this work. This demonstrates a higher fructose conversion over
4	UiO-66-SO ₃ H-W prepared via direct synthesis as compared to the post-synthesis
5	modification applied in [35], originating from the difference in the sulfonic acid groups
6	concentration. Moreover, faster reaction rates might be obtained using the UiO-66-SO ₃ H-
7	W catalyst, as 30 min are sufficient to reach fructose conversion and 5-HMF yield in the
8	range of the results reported at 100 °C after 1 h. Only one previous study, using NUS-6
9	(highly defective UiO-66-SO ₃ H), presented better results but with a stoichiometric
10	catalyst:fructose ratio [53].

Finally, the structural integrity of UiO-66-SO₃H-W, as viewed from XRD patterns in Figure S12, is preserved upon 6 h of catalytic tests up to 120 °C as all diffractograms conserved the ensemble of characteristic reflections of the as-made UiO-66-SO₃H-W. This implies a decent structural stability upon fructose dehydration in DMSO at high temperatures.

16 3.2.2. Catalyst recycling

In order to further evaluate the stability and reusability of UiO-66-SO₃H-W, nine
runs with the same catalyst were performed at 80 °C and 100 °C for 30 min. Figure 8
shows fructose conversion and 5-HMF yield after each run. These conditions were chosen
in order to eliminate the solvent effect so that the activity can be only attributed to the
catalyst.

After nine runs at 80 °C, fructose conversion and yield of 5-HMF reduced gradually from 48 to 25 % and from 18 to 3 %, respectively (Figure 8.a). Notably, from the third run, 5-HMF yield dropped to negligible 3 %, similar to that of the blank test run under the same conditions. The decrease of catalytic activity is typically attributed to the

adsorption of humins on the catalyst, hindering access to the active sites. Herein, their 1 2 presence is supported by FTIR-ATR analysis on UiO-66-SO₃H-W before and after 9 cycles at 80 °C (Figure S13). The spectra demonstrate a new broad band at ~1668 cm⁻¹ 3 which corresponds to C=C bond stretching in a furanic ring attributed to humins, while 4 the bands at ~951 and 1004 cm^{-1} might be indicative of adsorbed 5-HMF species on the 5 6 catalyst surface [61]. Moreover, remarkable deposition of humins on the catalyst after 9 7 cycles can be deduced from TGA, as compared to the fresh catalyst. As evident from Figure S14, the mass of the catalyst increased by ~19 % after recycling tests which is 8 9 attributed to the amount of humins adsorbed on the catalyst surface. Removal of thus-10 formed humins via thermal decomposition remains a problem for MOFs because of their 11 low (< 400 °C) thermal stability, and simple washing in conventional organic solvents under ultrasonic irradiation had no effect. 12



13

Figure 8. Conversion of fructose and yield of 5-HMF using UiO-66-SO₃H-W over
several runs. Conditions: 80 °C (a) and 100 °C (b) for 30 min.

A similar trend is observed upon recycling at 100 °C for 30 min (Figure 8.b). While the selectivity toward 5-HMF dropped significantly after the second run to reach (similar to the blank test), the fructose conversion remains almost quantitative which differs from the blank test. In parallel, the presence of an unknown compound, detected

by HPLC and attributed to soluble fructose oligomers [58], increases from the second 1 2 cycle. Therefore, at 100 °C the glucose conversion remains as high as ~100 % due to the 3 combined activity of DMSO and the surface acidity of the MOF, while the inner Brønsted acidity becomes inaccessible due to humins formation. For evaluation of a catalyst's 4 activity in fructose dehydration in DMSO it is critical to consider the solvent effect, which 5 is negligible at 80 °C and becomes considerable at 100 °C and above. Importantly, the 6 7 catalyst retained its structural integrity (Figure S15) under the given conditions even after 8 9 cycles which implies that the observed deactivation is not due to structural collapse of 9 the MOF structure but rather to the lack of accessibility of the sulfonic acid groups due 10 to the humins presence.

11 **4.** Conclusion

The direct synthesis of sulfonate-functionalized UiO-66-SO₃H nanocrystals in environmentally-friendly conditions was successfully made and applied to fructose dehydration. Replacement of hazardous and toxic DMF by water as the solvent led to an alteration of the crystal structure, switching the space group from *Fm-3m* to *Im-3*. Besides, the presence of Brønsted acidic -SO₃H groups lowered the available surface area through partial pore blocking effect by ~47 %, with a comparable effect on the pore volume (~49 %).

At 100 °C, it was shown that the UiO-66-SO₃H MOF prepared in DMF reached complete fructose conversion (> 98 %) after 2 h, barely surpassing the activity of the solvent itself, DMSO. On the other hand, the same MOF prepared in water (UiO-66-SO₃H-W) demonstrated complete fructose conversion already after 30 min under the same conditions. This catalyst showed high activity within the whole proposed range of temperatures (80-120 °C). Thus, at mild 80 °C, UiO-66-SO₃H-W demonstrated the decent 81 % fructose conversion and 52 % 5-HMF yield after 3 h while the blank test in DMSO
 showed no fructose conversion.

3 Additionally, UiO-66-SO₃H-W exhibited a well-pronounced structural stability. After 6 h of catalytic tests up to 120 °C, the catalyst retained its crystal structure. 4 Moreover, its structural integrity was proven by performing 9 consecutive catalytic runs 5 6 with no washing/drying steps between each run, simulating a continuous process with a 7 batch reactor. The catalyst gradually lost its activity towards 5-HMF formation with the 8 yield values dropping from 18 % to 3 %, as well as from 48 % to 14 % similar to those of the blank tests at 80 °C and 100 °C, respectively. Thus, it was shown that 80 °C is an 9 10 acceptable temperature to examine a catalyst's activity without the effect of DMSO. On the other hand, frequently reported fructose conversion and 5-HMF yield at 100 °C and 11 12 above should be attributed to the dual catalyst/DMSO activity.

1 ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at DOI: 10xxxx/xxxxx.

N₂ adsorption-desorption isotherms, SEM micrographs of MOF powders, NLDFT pore
size distribution calculated from N₂ isotherms, Photographs of solutions after test, HPLC
chromatograms of the solution, TGA thermographs before and after test, XPS spectrum
of UiO-66, Additional XRD patterns, FTIR-ATR spectra of the powders, and catalytic
results under different temperatures. The following files are available free of charge.

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1 **REFERENCES**

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- [1] Song, B.; Lin, R.; Ho, C.; Wu, H.; Tsui, T.; Yu, Y. Recent Advances and Challenges of Inter-Disciplinary Biomass Valorization by Integrating Hydrothermal and Biological Techniques. *Renew. Sustain. Energy Rev.* 2021, *135*, 110370. https://doi.org/10.1016/j.rser.2020.110370.
- Mondelli, C.; Gozaydın, G.; Yan, N.; Perez-Ramirez, J. Biomass Valorisation over
 Metal-Based Solid Catalysts from Nanoparticles to Single Atoms. *Chem. Soc. Rev.* 2020, 49, 3764–3782. https://doi.org/10.1039/d0cs00130a.
- [3] Ning, P.; Yang, G.; Hu, L.; Sun, J.; Shi, L.; Zhou, Y.; Wang, Z.; Yang, J.
 Biotechnology for Biofuels Recent Advances in the Valorization of Plant Biomass. *Biotechnol. Biofuels.* 2021, 14, 1–22. https://doi.org/10.1186/s13068-021-019493.
- [4] Esposito, D.; Antonietti, M. Redefining Biorefinery: the Search for
 Unconventional Building Blocks for Materials. *Chem. Soc. Rev.* 2015, 44, 5821–
 5835. https://doi.org/10.1039/c4cs00368c.
- [5] Rinaldi, R.; Schüth, F. Acid Hydrolysis of Cellulose as the Entry Point into
 Biorefinery Schemes. *ChemSusChem.* 2009, 2, 1096–1107.
 https://doi.org/10.1002/cssc.200900188.
- [6] Kang, S.; Fu, J.; Zhang, G. From Lignocellulosic Biomass to Levulinic Acid : A
 Review on Acid-Catalyzed Hydrolysis. *Renew. Sustain. Energy Rev.* 2018, 94,
 340–362. https://doi.org/10.1016/j.rser.2018.06.016.
- [7] Amin, F. R.; Khalid, H.; Zhang, H.; Rahman, S.; Zhang, R.; Liu, G.; Chen, C.
 Pretreatment Methods of Lignocellulosic Biomass for Anaerobic Digestion. *AMB Express.* 2017, 7, 72. https://doi.org/10.1186/s13568-017-0375-4.
- [8] Zhou, C.; Xia, X.; Lin, C.; Tong, D.; Beltramini, J. Catalytic Conversion of Lignocellulosic Biomass to Fine Chemicals and Fuels. *Chem. Soc. Rev.* 2011, 40, 5588–5617. https://doi.org/10.1039/c1cs15124j.
- [9] Vasic-Racki, D. History of Industrial Biotransformations Dreams and Realities,
 in: *Industrial Biotransformations*, 2nd ed., Wiley: Weinheim, Germany, 2006: pp.
 1–36.
- [10] Sajid, M.; Zhao, X.; Liu, D. Production of 2,5-Furandicarboxylic Acid (FDCA)
 from 5-Hydroxymethylfurfural (HMF): Recent Progress Focusing on the
 Chemical-Catalytic Routes. *Green Chem.* 2018, 20, 5427.
 https://doi.org/10.1039/c8gc02680g.
- [11] Garcia-Lopez, E. I.; Pomilla, F. R.; Megna, B.; Testa, M. L.; Liotta, L.F.; Marci,
 G. Catalytic Dehydration of Fructose to 5-Hydroxymethylfurfural in Aqueous
 Medium over Nb₂O₅-based Catalysts. Nanomaterials 2021, *11*, 1821.
 https://doi.org/10.3390/nano11071821.
 - 28

- Wang, H.; Kong, Q.; Wang, Y.; Deng, T.; Chen, C.; Hou, X.; Zhu, Y. Graphene 1 [12] 2 Oxide Catalyzed Dehydration of Fructose into 5-Hydroxymethylfurfural with 3 Isopropanol Cosolvent. ChemCatChem. 2014. 6. 728-732. as 4 https://doi.org/10.1002/cctc.201301067. 5
- [13] Sayed, M.; Warlin, N.; Hulteberg, C.; Munslow, I.; Lundmark, S.; Pajalic, O.;
 Tunå, P.; Zhang, B.; Pyo, S.; Hatti-kaul, R. 5-Hydroxymethylfurfural from
 Fructose: an Efficient Continuous Process in a Water-Dimethyl Carbonate
 Biphasic System with High Yield Product Recovery. *Green Chem.* 2020, 22, 5402.
 https://doi.org/10.1039/d0gc01422b.
- [14] Tao, F.; Song, H.; Chou, L. Dehydration of Fructose into 5-Hydroxymethylfurfural
 in Acidic Ionic Liquids. *RSC Adv.* 2011, *1*, 672–676.
 https://doi.org/10.1039/c1ra00088h.

11

15

20

26

31

35

39

44

- [15] Whitaker, M. R.; Parulkar, A.; Brunelli, N. A. Selective Production of 5Hydroxymethylfurfural from Fructose in the Presence of an Acid-Functionalized
 SBA-15 Catalyst Modified with a Sulfoxide Polymer. *Mol. Syst. Des. Eng.* 2020,
 5, 257–268. https://doi.org/10.1039/c9me00093c.
- 21 [16] Barbosa, S. L.; Freitas, M. D. S.; Santos, W. T. P.; Nelson, D. L.; Klein, S. I.; 22 Clososki, G. C.; Caires, F. J.; Baroni, A. C. M.; Wentz, A. P. Dehydration of D-Fructose in DMSO Using a Hydrophilic Sulfonated Silica Catalyst in a Process 23 Microwave Irradiation. Sci. Rep. 2021, 24 Promoted by 11, 1919. 25 https://doi.org/10.1038/s41598-020-80285-2.
- [17] Huang, Z.; Pan, Y.; Chao, Y.; Shen, W.; Wang, C.; Xu, H. Triazaheterocyclic
 Compound as an Efficient Catalyst for Dehydration of Fructose into 5Hydroxymethylfurfural. *RSC* Adv. 2014, 4, 13434.
 https://doi.org/10.1039/c4ra00534a.
- Jiang, N.; Huang, R.; Qi, W.; Su, R.; He, Z. Effect of Formic Acid on Conversion
 of Fructose to 5-Hydroxymethylfurfural in Aqueous/Butanol Media. *Bioenerg. Res.* 2012, *5*, 380–386. https://doi.org/10.1007/s12155-011-9141-7.
- [19] Kläusli, T. AVA Biochem: Commercialising Renewable Platform Chemical 5 HMF. *Green Process. Synth.* 2014, *3*, 235–236. https://doi.org/10.1515/gps-2014 0029.
- [20] Kruger, J. S.; Choudhary, V.; Nikolakis, V.; Vlachos, D. G. Elucidating the Roles of Zeolite H-BEA in Aqueous-Phase Fructose Dehydration and HMF Rehydration. *ACS Appl. Mater. Interfaces.* 2013, *3*, 1279–1291.
 https://doi.org/10.1021/cs4002157.
- 45 Qi, X.; Watanabe, M.; Aida, M.; Smith, R. L. Catalytic Dehydration of Fructose [21] into 5-Hydroxymethylfurfural by Ion-Exchange Resin in Mixed-Aqueous System 46 Microwave 2008, 799-805. 47 by Heating. Green Chem. 10, https://doi.org/10.1039/b801641k. 48
- 50 [22] Karimi, B.; Mirzaei, H. M. The Influence of Hydrophobic/Hydrophilic Balance of

1 2 2		the Mesoporous Solid Acid Catalysts in the Selective Dehydration of Fructose into HMF. <i>RSC Adv.</i> 2013 , <i>3</i> , 20655. https://doi.org/10.1039/c3ra44214d.
4 5 6 7	[23]	Shi, Y.; Li, X.; Hu, J.; Lu, J.; Ma, Y.; Zhang, Y.; Tang, Y. Zeolite Microspheres with Hierarchical Structures: Formation, Mechanism and Catalytic Performance. <i>J. Mater. Chem.</i> 2011 , <i>21</i> , 16223. https://doi.org/10.1039/c1jm11669j.
8 9 10 11 12	[24]	Guo, X.; Cao, Q.; Jiang, Y.; Guan, J.; Wang, X.; Mu, X. Selective Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Mesoporous SBA-15-SO ₃ H in Ionic Liquid BmimCl. <i>Carbohydr. Res.</i> 2012 , <i>351</i> , 35–41. https://doi.org/10.1016/j.carres.2012.01.003.
13 14 15 16	[25]	Shimizu, K.; Uozumi, R.; Satsuma, A. Enhanced Production of Hydroxymethylfurfural from Fructose with Solid Acid Catalysts by Simple Water Removal Methods. <i>Catal. Commun.</i> 2009 , <i>10</i> , 1849–1853. https://doi.org/10.1016/j.catcom.2009.06.012.
18 19 20 21 22	[26]	Morales, G.; Melero, J. A.; Paniagua, M.; Iglesias, J.; Hernández, B.; Sanz, M. Sulfonic Acid Heterogeneous Catalysts for Dehydration of C ₆ -Monosaccharides to 5-Hydroxymethylfurfural in Dimethyl Sulfoxide. <i>Chinese J. Catal.</i> 2014 , <i>35</i> , 644–655. https://doi.org/10.1016/S1872-2067(14)60020-6.
23 24 25 26 27	[27]	Bavykina, A.; Kolobov, N.; Khan, I. S.; Bau, J. A.; Ramirez, A.; Gascon, J. Metal-Organic Frameworks in Heterogeneous Catalysis: Recent Progress, New Trends, and Future Perspectives. <i>Chem. Rev.</i> 2020 , <i>120</i> , 8468–8535. https://doi.org/10.1021/acs.chemrev.9b00685.
28 29 30 31 32	[28]	Dias, E. M.; Petit, C. Towards the Use of Metal-Organic Frameworks for Water Reuse: a Review of the Recent Advances in the Field of Organic Pollutants Removal and Degradation and the Next Steps in the Field. <i>J. Mater. Chem. A.</i> 2015 , <i>3</i> , 22484–22506. https://doi.org/10.1039/C5TA05440K.
33 34 35 36	[29]	Barea, E.; Montoro, C.; Navarro, J. A. R. Toxic Gas Removal – Metal-Organic Frameworks for the Capture and Degradation of Toxic Gases and Vapours. <i>Chem. Soc. Rev.</i> 2014 , <i>43</i> , 5419–5430. https://doi.org/10.1039/c3cs60475f.
37 38 39 40 41	[30]	Shet, S. P.; Priya, S. S.; Sudhakar, K.; Tahir, M. A Review on Current Trends in Potential Use of Metal-Organic Framework for Hydrogen Storage. Int. J. Hydrogen Energy. 2021, 46, 11782–11803. https://doi.org/10.1016/j.ijhydene.2021.01.020.
42 43 44 45 46 47	[31]	Datta, S. J.; Mayoral, A.; Bettahalli, N. M. S.; Bhatt, P. M.; Karunakaran, M.; Carja, I. D.; Fan, D.; Mileo, P. G. M.; Semino, R.; Maurin, G.; Terasaki, O.; Eddaoudi, M. Rational Design of Mixed-Matrix Metal-Organic Framework Membranes for Molecular Separations. <i>Science</i> 2022 , <i>376</i> , 1080-1087. https://doi.org/10.1126/science.abe0192.
48 49 50	[32]	Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal-Organic Frameworks with Exceptional Stability. J. Am. Chem. Soc. 2008, 130,

1 2		13850–13851. https://doi.org/10.1021/ja8057953.
3 4 5 6	[33]	De Mello, D. M.; Tsapatsis, M. Selective Glucose to Fructose Isomerization over Modified Zirconium UiO-66 in Alcohol Media. <i>ChemCatChem.</i> 2018 , <i>10</i> , 2417– 2423. https://doi.org/10.1002/cctc.201800371.
7 8 9 10 11	[34]	Oozeerally, A. R.; Burnett, D. L.; Chamberlain, T. W.; Walton, R. I.; Degirmenci, V. Exceptionally Efficient and Recyclable Heterogeneous Metal-Organic Framework Catalyst for Glucose Isomerization in Water. <i>ChemCatChem.</i> 2018 , <i>10</i> , 706–709. https://doi.org/10.1002/cctc.201701825.
12 13 14 15 16	[35]	Chen, J.; Li, K.; Chen, L.; Liu, R.; Huang, X.; Ye, D. Conversion of Fructose into 5-Hydroxymethylfurfural Catalyzed by Recyclable Sulfonic Acid-Functionalized Metal-Organic Frameworks. <i>Green Chem.</i> 2014 , <i>16</i> , 2490. https://doi.org/10.1039/c3gc42414f.
17 18 19 20	[36]	Kim, T. H.; Kim, S. G. Clinical Outcomes of Occupational Exposure to N,N-Dimethylformamide: Perspectives from Experimental Toxicology. <i>Saf. Health Work.</i> 2011 , <i>2</i> , 97–104. https://doi.org/10.5491/SHAW.2011.2.2.97.
21 22 23 24 25	[37]	Foo, M. L.; Horike, S.; Fukushima, T.; Hijikata, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. Ligand-Based Solid Solution Approach to Stabilisation of Sulphonic Acid Groups in Porous Coordination Polymer Zr ₆ O ₄ (OH) ₄ (BDC) ₆ (UiO-66). <i>Dalt. Trans.</i> 2012 , <i>41</i> , 13791–13794. https://doi.org/10.1039/c2dt31195j.
26 27 28 29 30	[38]	Biswas, S.; Zhang, J.; Li, Z.; Liu, Y.; Grzywa, M.; Sun, L.; Volkmer, D.; Van Der Voort, P. Enhanced Selectivity of CO ₂ over CH ₄ in Sulphonate-, Carboxylate- and Iodo-Functionalized UiO-66 Frameworks. <i>Dalt. Trans.</i> 2013 , <i>42</i> , 4730–4737. https://doi.org/10.1039/c3dt32288b.
31 32 33 34 35	[39]	Piscopo, C. G.; Polyzoidis, A.; Schwarzer, M.; Loebbecke, S. Stability of UiO-66 under Acidic Treatment: Opportunities and Limitations for Post-Synthetic Modifications. <i>Microporous Mesoporous Mater.</i> 2015 , <i>208</i> , 30–35. https://doi.org/10.1016/j.micromeso.2015.01.032.
36 37 38	[40]	Reinsch, H. "Green" Synthesis of Metal-Organic Frameworks. <i>Eur. J. Inorg. Chem.</i> 2016, 2016, 4290–4299. https://doi.org/10.1002/ejic.201600286.
 39 40 41 42 43 	[41]	Zhang, J.; White, G.; Ryan, M.; Hunt, A. J.; Katz, M. J. Dihydrolevoglucosenone (Cyrene) as a Green Alternative to N,N-Dimethylformamide (DMF) in MOF Synthesis. <i>ACS Sustain. Chem. Eng.</i> 2016 , <i>4</i> , 7186–7192. https://doi.org/10.1021/acssuschemeng.6b02115.
44 45 46 47 48	[42]	Khabzina, Y.; Dhainaut, J.; Ahlhelm, M.; Richter, H.; Reinsch, H.; Stock, N.; Farrusseng, D. Synthesis and Shaping Scale-up Study of Functionalized UiO-66 MOF for Ammonia Air Purification Filters. <i>Ind. Eng. Chem. Res.</i> 2018 , <i>57</i> , 8200–8208. https://doi.org/10.1021/acs.iecr.8b00808.
49 50	[43]	Avci-Camur, C.; Perez-Carvajal, J.; Imaz, I.; Maspoch, D. Metal Acetylacetonates as a Source of Metals for Aqueous Synthesis of Metal-Organic Frameworks. <i>ACS</i>

1 2 2		Sustain. https://doi.org/	<i>Chem</i> . 10.1021/acssus	<i>Eng</i> . schemeng.8b	2018 , 003180.	6,	14554–14560.
3 4 5 6 7	[44]	Dai, S.; Nouar, Synthesis of M Int. Ed. 2021, 6	, F.; Zhang, S.; Ietal(IV) Carbo 50, 4282–4288.	Serre, C. C al-Organic 1 org/10.1002	One-Step Ro Framework /anie.20201	oom-Temperature s. <i>Angew. Chem.</i> 4184.	
8 9 10 11 12 13	[45]	Chen, Z.; Wang T.; Farha, O. Functionalized Removal. https://doi.org/	g, X.; Noh, H.; K. Scalable, R Zirconium-Ba <i>CrystEngCo</i> 10.1039/c9ce00	Ayoub, G.; I Room Temp sed Metal-C <i>omm</i> . 0213h.	Peterson, G. erature, and rganic Fran 2019 ,	W.; Buru, Water-Ba neworks for 21,	C. T.; Islamoglu, sed Synthesis of Toxic Chemical 2409–2415.
14 15 16 17	[46]	Reinsch, H.; B Vos, D. Green https://doi.org/	ueken, B.; Ver Synthesis of 2 10.1039/c5ce00	rmoortele, F Zirconium-M 0618j.	.; Stassen, I 10Fs. <i>Cryst</i>	.; Lieb, A.; tEngComm.	Lillerud, K.; De 2015 , <i>17</i> , 4070.
18 19 20 21	[47]	Hu, Z.; Peng, Y Approach for the 4862–4868. htt	'.; Kang, Z.; Qi ne Facile Synth ps://doi.org/10	an, Y.; Zhao nesis of UiO .1021/acs.in	o, D. A Mod 66-Type M orgchem.5b	ulated Hyd OFs. <i>Inorg.</i> 00435.	rothermal (MHT) <i>Chem.</i> 2015 , <i>54</i> ,
22 23 24 25	[48]	Chen, Z.; Wa Functionalized Ethanol Adsorp	ung, X.; Islan Zirconium-Ba otion. <i>Inorgani</i>	noglu, T.; ased Metal <i>cs.</i> 2019 , 7,	Farha, O. -Organic F 56.	K. Green Framework	Synthesis of a for Water and
26 27 28 29 30	[49]	Taylor, J. M.; H Role of a Three Sulfonated Me 11506. https://d	Komatsu, T.; Dee Dimensiona etal-Organic Fr loi.org/10.1021	ekura, S.; O Illy Ordered amework. J I/jacs.5b072	tsubo, K.; T Defect Sul <i>I. Am. Chet</i> 67.	akata, M.; blattice on <i>m. Soc.</i> 20	Kitagawa, H. The the Acidity of a 15 , <i>137</i> , 11498–
31 32 33 34 35	[50]	Kandiah, M.; I Larabi, C.; Qu Stability of Ta https://doi.org/	Nilsen, M. H.; adrelli, E. A.; agged UiO-66 10.1021/cm102	Usseglio, S Bonino, F.; Zr-MOFs. 2601v.	.; Jakobsen Lillerud K <i>Chem. Ma</i>	, S.; Olsby . P.; Lyon <i>uter</i> . 2010 ,	e, U.; Tilset, M.; D. Synthesis and 22, 6632–6640.
36 37 38 39 40 41	[51]	De Mello, M. I S.; Li, X.; Vla Phosphonate-M Decyclization o 2020 , <i>59</i> , 1326	D.; Kumar, G.; chos, D. G.; H lodified UiO-6 of 2-Methyltetr 0–13266. https	Tabassum, ' Han, S.; Sco 66 Brønsted rahydrofurar :://doi.org/10	T.; Jain, S. 1 tt, S.; Daue Acid Catal to Pentadio .1002/anie.	K.; Chen T. enhauer, P. yst and its enes. <i>Angev</i> 202001332	-H., Caratzoulas, J.; Tsapatsis, M. Use in Dehydra- w. Chem. Int. Ed.
42 43 44 45	[52]	Juan-Alcaniz, J P.; Devic, T.; C – Catalytic Pert <i>Technol.</i> 2013 ,	:; Gielisse, R.; Guillou, N.; Ser formance of Su <i>3</i> , 2311–2318.	Lago, A. B.; rre, C.; Kapt lfonic Acid https://doi.o	Ramos-Fer eijn, F.; Gas Functionaliz org/10.1039	nandez, E. scon J. Tow zed Archite /c3cy00272	V.; Serra-Crespo, vards Acid MOFs ctures. <i>Catal. Sci.</i> 2a.
47 48 49 50	[53]	Hu, Z.; Peng, Y Babarao, R.; V Porous Metal- Acidity: The	7.; Gao, Y.; Qia Vang, Y.; Yan Organic Framo Decisive Role	an, Y.; Ying n, N.; Zhao, eworks with of Hafniun	, S.; Yuan, D. Direct High Sta n in Effici	D.; Horike, Synthesis bility and ent and Se	S.; Ogiwara, N.; of Hierarchically Strong Brønsted elective Fructose

28, 1 Dehydration. Chem. Mater. 2016. 2659-2667. 2 https://doi.org/10.1021/acs.chemmater.6b00139 3 4 Hasan, Z.; Khan, N. A.; Jhung, S. H. Adsorptive Removal of Diclofenac Sodium [54] from Water with Zr-Based Metal-Organic Frameworks. Chem. Eng. J. 2015, 284, 5 6 1406–1413. https://doi.org/10.1016/j.cej.2015.08.087. 7 8 Chavan, S. M.; Shearer, G. C.; Svelle, S.; Olsbye, U.; Bonino, F.; Ethiraj, J.; [55] 9 Lillerud, K. P.; Bordiga, S. Synthesis and Characterization of Amine-Functionalized Mixed-Ligand Metal-Organic Frameworks of UiO-66 Topology. 10 Inorg. Chem. 2014, 53, 9509–9515. 11 12 Shearer, G. C.; Chavan, S.; Bordiga, S.; Svelle, S.; Olsbye, U.; Lillerud, K. P. 13 [56] Defect Engineering: Tuning the Porosity and Composition of the Metal-Organic 14 Framework UiO-66 via Modulated Synthesis. Chem. Mater. 2016, 28, 3749–3761. 15 16 https://doi.org/10.1021/acs.chemmater.6b00602. 17 18 Melero, J. A.; Bautista, L. F.; Iglesias, J.; Morales, G.; Sánchez-Vásquez, R.; [57] 19 Wilson, K.; Lee, A. F. New Insights in the Deactivation of Sulfonic Modified SBA-15 Catalysts for Biodiesel Production from Low-grade Oleaginous Feedstock. 20 21 Appl. Catal. *A*: General. 2014, 488, 111-118. 22 https://doi.org/10.1016/j.apcata.2014.09.023. 23 Kılıc, E.; Yılmaz, S. Fructose Dehydration to 5-Hydroxymethylfurfural over 24 [58] Sulfated TiO₂-SiO₂, Ti-SBA-15, ZrO₂, SiO₂, and Activated Carbon Catalysts. Ind. 25 Eng. Chem. Res. 2015, 54, 5220–5225. https://doi.org/10.1021/acs.iecr.5b00628. 26 27 Sengwa, R. J.; Sankhla, S.; Khatri, V. Dielectric Characterization and Molecular 28 [59] 29 Interaction Behaviour in Binary Mixtures of Amides with Dimethylsulphoxide and 1.4-Dioxane. Mol. 2010. 151, 17-22. 30 J. Liq. https://doi.org/10.1016/j.molliq.2009.10.011. 31 32 Fachri, B. A.; Abdilla, R.; Bovenkamp, H.; Rasrendra, C.; Heeres H. J. 33 [60] 34 Experimental and Kinetic Modeling Studies on the Sulphuric Acid Catalyzed 35 Conversion of D-Fructose to 5-Hydroxymethylfurfural and Levulinic acid in ACS Chem. Eng. 2015, 36 Water. Sustain. 3, 3024–3034. https://doi.org/10.1021/acssuschemeng.5b00023. 37 38 Tsilomelekis, G.; Orella, M. J.; Lin, Z.; Cheng, Z.; Zheng, W.; Nikolakis, V.; 39 [61] Vlachos, D. G. Molecular Structure, Morphology and Growth Mechanisms and 40 41 Rates of 5-Hydroxymethylfurfural (HMF) Derived Humins. Green Chem. 2016, 18, 1983–1993. https://doi.org/10.1039/c5gc01938a. 42 43