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Bakytzhan Yeskendir, Priscilla Magalhaes de Souza, Pardis Simon, Robert Wojcieszak, Christian Courtois, et al.. Water-Based Synthesis of Zr6-Based Metal–Organic Framework Nanocrystals with Sulfonate Functions: Structural Features and Application to Fructose Dehydration. ACS Applied Nano Materials, 2022, ACS Applied Nano Materials, 10.1021/acsanm.2c02916 . hal-03794329

HAL Id: hal-03794329

<https://hal.univ-lille.fr/hal-03794329>

Submitted on 3 Oct 2022

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

5

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1 **Abstract**

2 A series of zirconium-based Metal-Organic Framework (MOF) nanocrystals (95-211 nm)
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
11 DMF showed only 30 % fructose conversion. Moreover, intrinsic catalytic effect at 80 °C
12 was only observed with the water-based UiO-66-SO₃H. Without reactivation of the
13 catalyst, recycling tests demonstrated the preservation of its structural integrity upon 9
14 consecutive cycles, while a gradual loss of the catalyst activity was attributed to the
15 humins adsorption on the MOFs.

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

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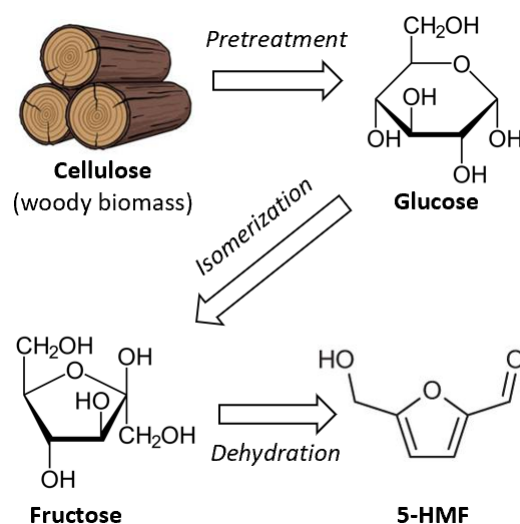
1. Introduction

The studies on conversion of biomass into fine chemicals and fuels has significantly increased over the past years highlighting biomass as a sustainable feedstock for the production of a variety of valuable chemicals [1–3]. Lignocellulosic biomass is of particular interest, as it does not compete with food production. Generally, lignocellulosic biomass consists of three major polymeric components: lignin (~25 %), cellulose (~45 %) 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 allows to obtain convertible sugar monomers from carbohydrate polymers in a cost-effective way, however technologically challenging at large scale. Other pretreatment technologies include physical (mechanical, ultrasound, microwave), chemical (acid, alkaline), and biological (microbes, enzymes) methods [7]. Thereafter, many reactions may be performed to convert the sugar monomers into more valuable products, such as hydrogenation, isomerization, and deoxygenation [8]. Specifically, fructose is the product 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.

1 Generally, dehydration of fructose itself is catalyzed by Brønsted acids. For instance,
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
4 obtained when formic acid was used as the catalyst in a water/n-butanol mixture at 170
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.



11
12 **Figure 1.** General process pathway towards production of 5-HMF from lignocellulosic
13 biomass.

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

1 HMF yield after 1 h at 120 °C in ionic liquid [BMIM]Cl [24]. Complete fructose
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
4 increase of the product yield [25]. Additionally, remarkable 100 % fructose conversion
5 and 93 % 5-HMF yield were obtained also in DMSO after 1 h over Amberlyst-70 at 140
6 °C [26]. It should be noted that such high temperatures (≥ 120 °C) hinder the cost-
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
12 unique combination of large surface area, controllable pore size as well as high
13 physicochemical properties tunability, they have been used in various applications such
14 as heterogeneous catalysis [27], waste-water purification [28], toxic gas removal [29] and
15 gas storage [30], sometimes even unveiling performances unreachable by conventional
16 porous solids [31].

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

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

7 Similarly, direct fructose dehydration into 5-HMF over MOFs with sulfonic acid
8 functions leads to a considerable increase in conversion and product yield. Thus, the post-
9 synthetic functionalization of MIL-101(Cr) led to complete fructose conversion with 90
10 % 5-HMF yield in 1 h at 120 °C, whereas the non-functionalized MOF exhibited a
11 fructose conversion of 45 % and 5-HMF yield of 24 % [35].

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

1 Particularly, green and scalable syntheses of UiO-66-based functionalized MOFs have
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
4 chemical properties of conventional porous solids such as zeolites, carbons or silicas is
5 more complex as compared to the MOFs, especially in green conditions. Therefore, the
6 list of UiO-66-X prepared in water includes the following nominations: UiO-66-COOH
7 [42–44], UiO-66-(COOH)₂ [43,45–47], UiO-66-(COOH)₄ [47], UiO-66-NH₂
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,
12 varying the Zr-source also leads to porous MOFs with decent available surface areas.
13 Therefore, the present work is exploring water-based synthesis of UiO-66-SO₃H MOF
14 with emphasis on synthesis condition optimization and the resulting physicochemical
15 properties, as well as its performance in fructose dehydration to 5-HMF with respect to
16 UiO-66-SO₃H prepared in DMF. UiO-66 was chosen as the target MOF due to its good
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
20 conditions, was also investigated.

21 **2. Experimental**

22 **2.1 Materials**

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

1 (pure, Carlo Erba Reagents), dimethyl sulfoxide (99.7 %, Fisher BioReagents), acetic acid
2 (100 %, VWR), ethanol (96 %, VWR), and 5-(hydroxymethyl)furfural (98 %, Acros
3 Organics) were used as-received.

4 **2.2 Catalysts preparation**

5 UiO-66 was synthesized following the methodology previously described by Foo
6 *et al.* [37]. Namely, 0.32 g of $ZrCl_4$ and 0.22 g of terephthalic acid (molar ratio of 1:1)
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.
12 Eventually, the product was recovered and dried overnight at 100 °C.

13 The preparation of UiO-66-SO₃H-D was done similarly, by dissolving 0.31 g of
14 $ZrCl_4$ and 0.35 g of monosodium 2-sulfoterephthalate (molar ratio of 1:1) and adding
15 acetic acid in 100 mL of DMF. All other steps are identical as in the case of UiO-66. For
16 comparison, a material with a molar ratio of 1:2 was also prepared.

17 For UiO-66-SO₃H-W preparation, 1 g of $Zr(SO_4)_2 \cdot 4H_2O$ and 1.44 g of
18 monosodium 2-sulfoterephthalate (molar ratio of 1:2) were dissolved in 100 mL of water.
19 The resulting solution was heated up to 100 °C under reflux, as a simpler alternative to
20 solvothermal conditions. The resulting white solid was recovered and washed 3 times
21 with fresh H₂O as well as with ethanol at 50 °C overnight. Upon washing, the product
22 was dried at 100 °C overnight. For comparison, materials with a molar ratio of 1:1 and
23 with either $ZrCl_4$ or $Zr(SO_4)_2 \cdot 4H_2O$ were also prepared.

24 **2.3 Catalysts characterization**

1 Powder X-Ray Diffraction (XRD) patterns were recorded on a D8 Advance
2 instrument from Bruker, equipped with a $\text{CuK}\alpha$ X-ray source ($\lambda = 1.54184 \text{ \AA}$), using the
3 following parameters: 2θ range between $5\text{-}40^\circ$, scan rate of $0.02^\circ/\text{step}$, and acquisition
4 time of $1 \text{ s}/\text{step}$. The simulated pattern of $\text{UiO-66-SO}_3\text{H}$ was plotted using its CIF file
5 provided by Taylor *et al.* [49].

6 Textural properties were measured by N_2 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 ($p/p_0 = 0.1\text{-}$
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 (NLDFIT) model.

13 Scanning electron micrographs were registered on a JEOL JSM 6700F microscope
14 in the range of $5\text{-}10 \text{ kV}$. Before observation under microscope, the samples were covered
15 with a thin layer of Cr (150 \AA).

16 Infrared spectra (IR) were measured on a Perkin–Elmer “Spectrum Two”
17 spectrometer equipped with a diamond and operating in the attenuated total reflectance
18 (ATR) mode between 4000 and 400 cm^{-1} .

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

23 X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a Kratos
24 Axis Ultra DLD instrument equipped with a monochromatized $\text{AlK}\alpha$ X-ray source
25 powered at 225 W (15 mA , 15 kV). The base pressure in the analysis chamber was lower

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

7 Thermogravimetric analysis (TGA) profiles were obtained with a thermal
8 analyzer instrument Q600 from TA Instrument within the temperature range 25 – 800 °C
9 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
11 Plasma – Optical Emission Spectroscopy (ICP-OES). Analyses were performed on a
12 Perkin Elmer Optima 2000 DV instrument to determine the chemical composition of the
13 solids based on Zr, S and Na. Before analysis, a known
14 amount of sample was dissolved in a diluted HF-HCl solution, and then heated under
15 microwave until complete dissolution.

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

21 **2.4. Catalytic tests**

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

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

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

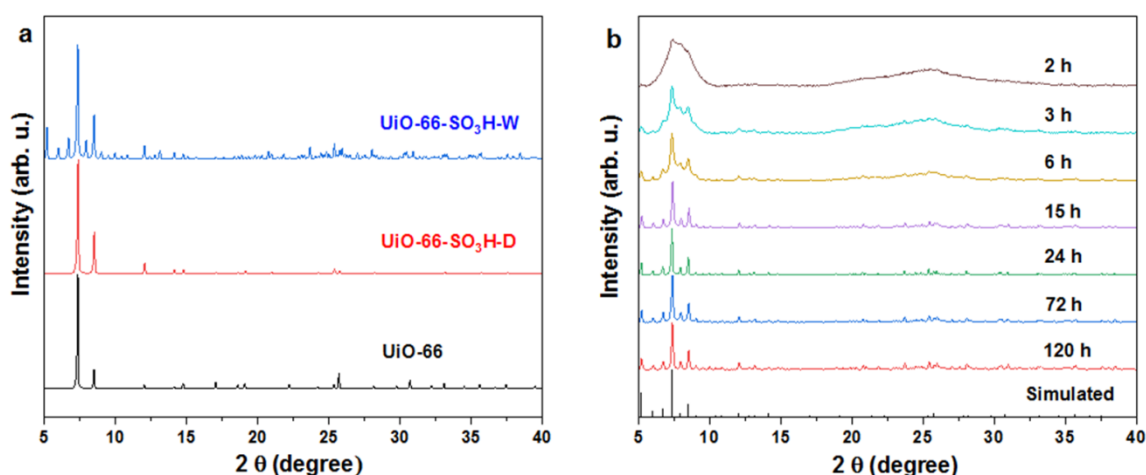
$$10 \quad \textbf{Yield} (\%) = \frac{\text{mol of HMF}}{\text{mol of Fructose}_i} \quad (2)$$

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-
15 66-SO₃H-W). It appears that a ratio of 1:2 was necessary to obtain a highly crystalline
16 sulfonic-functionalized MOF in water, while from a ratio of 1:1 the obtained UiO-66 and
17 UiO-66-SO₃H-D were of similar crystallinity. Owing to the difficulty to activate MOFs
18 with large amounts of linkers trapped within their porosity, only the ratio of 1:1 will be
19 considered next for the MOFs synthesized in DMF. As expected, the prepared UiO-66
20 exhibits characteristic reflections at approximately 7.4, 8.4 and 25.5 ° (2θ) corresponding
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 -
23 SO₃H groups does not change the topology of the resulting MOF: a face-centered cubic

1 organization in the unit cell ($Fm-3m$ space group, $a = 20.7004 \text{ \AA}$). Interestingly, the
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
4 topology representing a cubic organization with a doubled unit cell parameter ($Im-3$, $a =$
5 41.4906 \AA) and a lowered crystallographic symmetry [49,52]. This phenomenon is related
6 to a large number of structural defects, with only 8 linkers coordinating the Zr₆ clusters
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

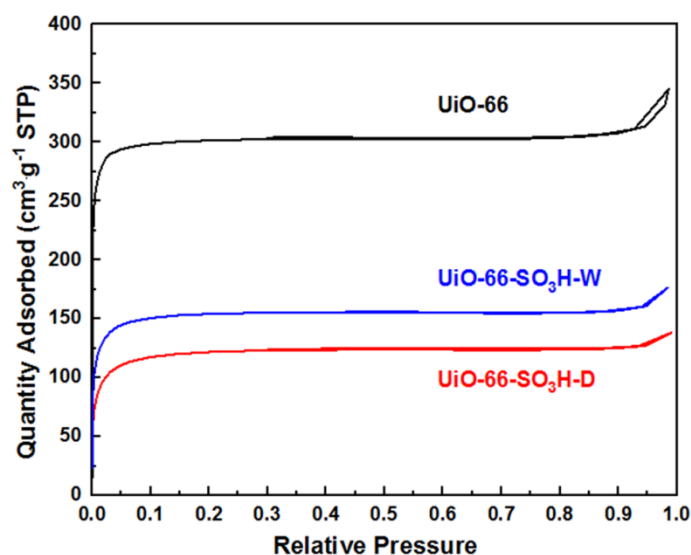
12 **Figure 2.** XRD patterns of UiO-66, UiO-66-SO₃H-D and UiO-66-SO₃H-W (a) and UiO-
13 66-SO₃H-W prepared in water with various synthesis durations (b).

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

1 Such tendency is in agreement with the results obtained by N₂ porosimetry
2 analysis. N₂-sorption isotherms are given in Figure S2 and the related data are provided
3 in Table S2. A successive increase of adsorbed N₂ in the micropore region is observed
4 upon crystallization time, hence leading to higher available surface areas and confirming
5 the obtention of better crystallized microporous materials. Of note, a small N₂ uptake at
6 high partial pressures (p/p_0) indicates the presence of intercrystalline porosity which is
7 generally observed with small crystals. Owing to its decent yield and S_{BET} , only the UiO-
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
11 adsorption/desorption isotherms, with a plateau at low relative pressures ($p/p_0 < 0.2$) for
12 all studied solids, are characteristic of microporous materials. The slight uptake observed
13 at high relative pressure ($p/p_0 > 0.9$) is typical of intercrystalline porosity for
14 nanomaterials. Furthermore, the presence of sulfonic acid functions may be deduced from
15 the significantly lower nitrogen adsorbed at any partial pressure, as the functions occupy
16 an important space within the porosity of the MOF. As seen in Table 1, the non-
17 functionalized UiO-66 exhibits the highest specific surface area ($1206 \text{ m}^2\cdot\text{g}^{-1}$) and
18 micropore volume ($0.47 \text{ cm}^3\cdot\text{g}^{-1}$) as opposed to the UiO-66-SO₃H materials. The
19 synthesis of UiO-66-SO₃H in DMF leads to a significant decrease of about 60 % in
20 specific surface area ($468 \text{ m}^2\cdot\text{g}^{-1}$) and micropore volume ($0.19 \text{ cm}^3\cdot\text{g}^{-1}$). Of note, Biswas
21 *et al.* also prepared UiO-66-SO₃H in DMF and obtained a specific Langmuir surface area
22 of $769 \text{ m}^2\cdot\text{g}^{-1}$ and a micropore volume of $0.26 \text{ cm}^3\cdot\text{g}^{-1}$ [39]. Herein, when DMF is replaced
23 by water, a micropore volume of $0.26 \text{ cm}^3\cdot\text{g}^{-1}$ is also obtained along with a BET surface
24 area of $639 \text{ m}^2\cdot\text{g}^{-1}$ (-47 % as compared to the reference UiO-66) after 24 hours of
25 crystallization time. After 72 hours, the resulting BET surface area ($630 \text{ m}^2\cdot\text{g}^{-1}$) remains

1 within the experimental and apparatus errors ($\pm 5 \text{ m}^2\cdot\text{g}^{-1}$). Regarding the pore size
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
4 around 0.6 nm [32], which could not be probed by the apparatus used. Therefore, the use
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.



9

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

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

1 0.41 mmol·g⁻¹, underlining that direct synthesis seems a better method to obtain more
 2 acidic catalysts.

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

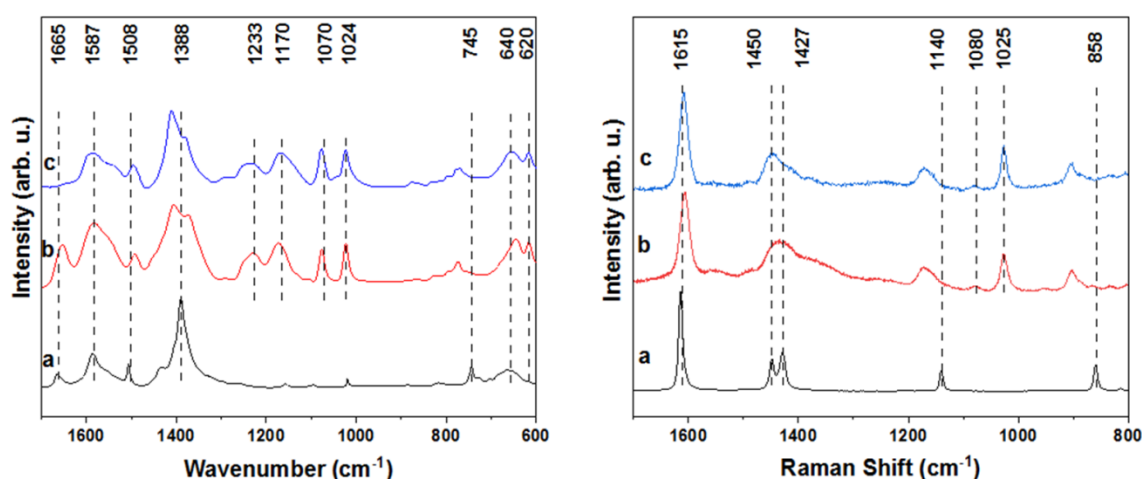
Catalysts	S _{BET} (m ² ·g ⁻¹)	V _{total} (cm ³ ·g ⁻¹) ^a	V _{micro} (cm ³ ·g ⁻¹)	Acid sites density ^b (mmol·g ⁻¹) (μmol·m ⁻²)	
UiO-66	1206	0.53	0.47	-	-
UiO-66-SO ₃ H-D	468 (-61 %)	0.21 (-60 %)	0.19 (-60 %)	0.49	1.05
UiO-66-SO ₃ H-W	639 (-47 %)	0.27 (-49 %)	0.26 (-45 %)	0.77	1.21

4 ^a Derived from adsorption branch of isotherms at p/p₀ = 0.99;

5 ^b Estimated by acid-base titration.

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

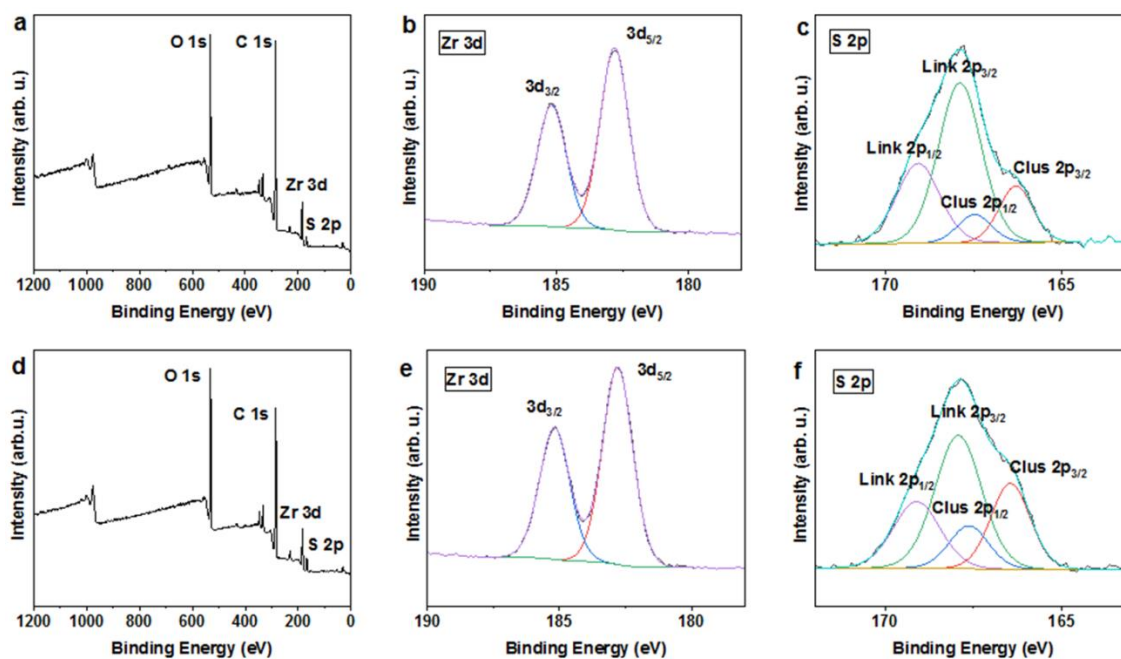
1 vibrations (~ 1170 and 1233 cm^{-1}), which are coherent with the Raman bands at 1025 cm^{-1}
 2 1 and 1080 cm^{-1} , respectively [35,54]. Besides, the Raman bands at 1140 and 858 cm^{-1}
 3 correspond to the breathing mode of the linker and C-H in-plane bending, respectively.
 4 Importantly, there is also the IR band characteristic of C=O stretching at $\sim 1665\text{ cm}^{-1}$ in
 5 both UiO-66 and UiO-66-SO₃H-D, which allows tracing DMF by its carbonyl group [55].
 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.



12
 13 **Figure. 4** FTIR-ATR (left) and Raman (right) spectra of the synthesized MOFs: a – UiO-
 14 66, b – UiO-66-SO₃H-D, c – UiO-66-SO₃H-W.

15 The crystal morphology of all the studied materials was visualized by SEM, and
 16 representative images are given in Figure S5. The classical UiO-66 is constituted of well-
 17 faceted, octahedrally-shaped nanocrystals with a narrow particle size distribution around
 18 132 nm. At the same time, the two sulfonated analogues exhibit distorted nanocrystals
 19 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.



3
4 **Figure 5.** XPS spectra of the as-synthesized solids: UiO-66-SO₃H-D survey (a), Zr 3d (b)
5 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
8 measurements (Figure S6) using a method described by Shearer *et al.* [56]. Accordingly,
9 the classical UiO-66 exhibited one missing terephthalate ligand per Zr₆-cluster while the
10 two functionalized MOFs surprisingly exhibited approximately 2.3 missing ligands per
11 cluster. These results were further supported by ICP elemental analysis, according to
12 which UiO-66-SO₃H-D and UiO-66-SO₃H-W had 1.51 and 1.41 zirconium atoms per
13 sulfur atom, respectively. This, in turn, suggests that UiO-66-SO₃H-D would actually be
14 slightly more defective than UiO-66-SO₃H-W, owing to the large concentration of
15 modulators (acetate from acetic acid and formate from DMF degradation) in the synthesis
16 mixture. Accordingly, the Zr/S surface atomic ratios derived from XPS analysis of UiO-
17 66-SO₃H-D and UiO-66-SO₃H-W are 1.60 and 1.46, respectively (Figure 5). This agrees

1 well with previous studies [49]. The resulting molecular formula of UiO-66-SO₃H-W is
 2 thus Zr₆O₄(OH)₄[C₆H₃(COO)₂SO₃H]_{4.3}.

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

Catalysts	D _c (nm) ^a	D _p (nm) ^b	Zr/S atomic ratio		Missing linkers per Zr-cluster ^d
			ICP	XPS ^c	
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

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

7 Examination of UiO-66 S 2p (Figure S7) spectrum reveals that in this material,
 8 which is free of -SO₃H moieties, sulfur traces were found. The spectrum was decomposed
 9 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
 10 centered at 166.9 eV. This contribution is attributed to a Cluster-bound sulfur from
 11 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.

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

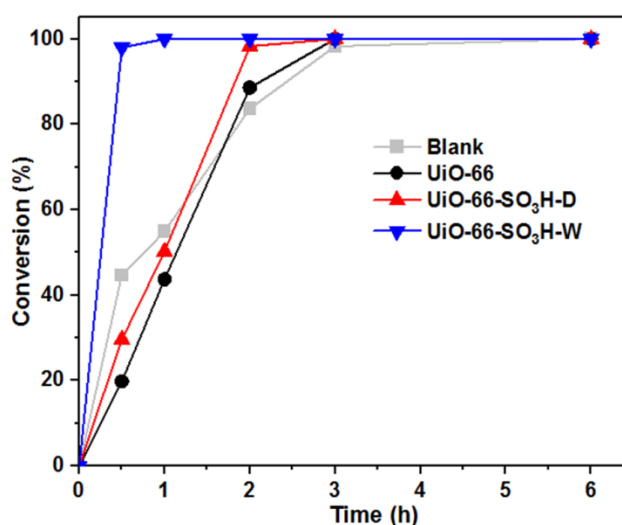
1 impact the acid titration as it is not selective toward sulfonate moieties. Especially, the
2 relative proportion of S species bound to Zr_6 -clusters seems higher in UiO-66-SO₃H-W
3 as compared to UiO-66-SO₃H-D, which could be due to the use of zirconium sulfate as a
4 synthesis precursor. Lastly, supported by the absence of a contribution centered at 1071.5
5 eV on the survey spectra, no sodium was detected implying the complete *in-situ* -SO₃Na
6 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
12 are able to convert fructose to 5-HMF at 100 °C [35,58]. Notably, the two catalysts
13 prepared in DMF (UiO-66 and UiO-66-SO₃H-D) exhibited approximately the same
14 conversion profiles as the blank test, indicating that they possess a low activity under
15 these reaction conditions. Instead, UiO-66-SO₃H-W catalyst achieved the complete
16 conversion of fructose (> 98 %) already after 30 minutes confirming its superior activity,
17 while it remained around 20 % for UiO-66, 30 % for UiO-66-SO₃H-D catalysts and 45
18 % in DMSO alone.

19 The presence of residual DMF within the porosity of UiO-66-SO₃H-D, as detected
20 by FTIR spectroscopy, may hinder fructose from reaching the Brønsted acid sites.
21 Especially, DMF was always present on the chromatograms upon analyzing the reaction
22 products when the MOFs prepared in DMF were used as catalysts, while it was absent
23 when using UiO-66-SO₃H-W (Figure S8). An additional blank test was conducted with a
24 mixture of DMSO and DMF (3:1 v:v). As a result, no fructose was converted after 2 h at
25 100 °C in the presence of DMF, as supported by the colorless reaction solution, while 80

1 % of fructose was converted in DMSO alone yielding a light-brown colored solution
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
4 through S and O atoms on DMSO over a wide range of concentrations [59]. The decreased
5 initial fructose conversion rates over UiO-66 and especially UiO-66-SO₃H-D may hence
6 be attributed to the release of DMF in the mixture. Nevertheless, as it is evident from
7 Figure 6 after 2 h, fructose conversion over UiO-66-SO₃H-D surpasses that of the blank
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
13 **Figure 6.** Conversion of fructose at 100 °C as a function of reaction time over different
14 catalysts (UiO-66, UiO-66-SO₃H-D and UiO-66-SO₃H-W) and blank test (without
15 catalyst).

16 Although UiO-66-SO₃H-W is the most efficient catalyst of the series for
17 converting fructose into 5-HMF, the suppressive effect of DMF present in the catalysts
18 prevent from discussing the effect of the acid site density. While the objective of this
19 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.

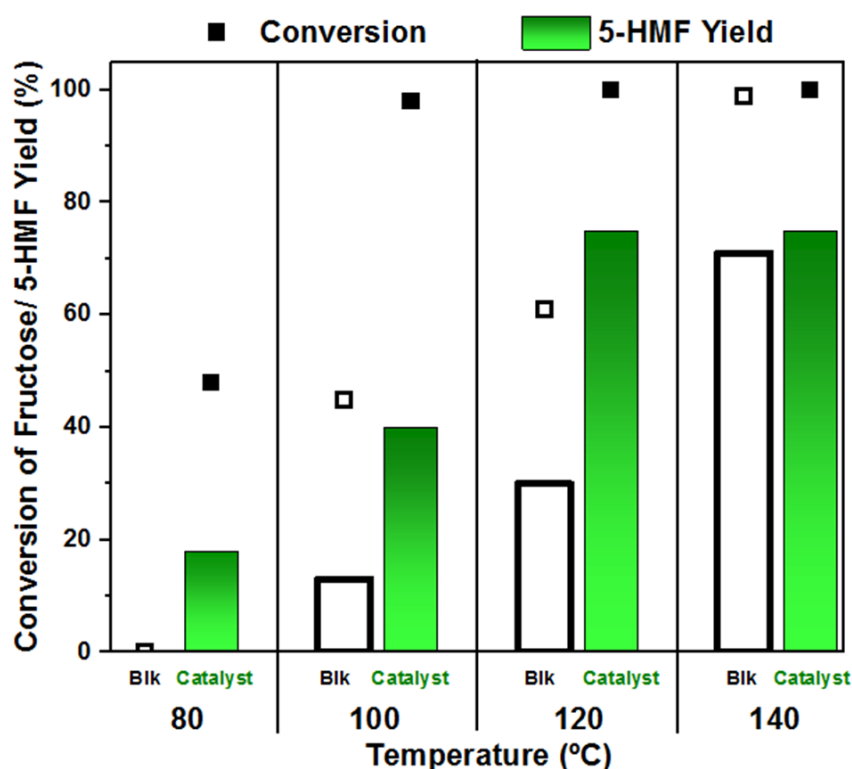
3 **3.2.1. Effect of reaction temperature**

4 The effect of temperature (80-140 °C) on the performance of the catalysts in
5 fructose dehydration was further evaluated over UiO-66-SO₃H-W. Figure 7 compares the
6 fructose conversion and yield of 5-HMF after 30 min of reaction carried out with or
7 without UiO-66-SO₃H-W at different temperatures. Furthermore, the related full kinetic
8 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
12 and with the catalyst. Furthermore, the liquids after reaction showed an intense brown
13 color, in spite of a similar amount of 5-HMF, approximately 75 % of yield. A significant
14 part of the remaining 25 % are constituted of soluble fructose oligomers and insoluble
15 humins which are undetectable by HPLC. These compounds are formed from both
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).
19 Interestingly, UiO-66-SO₃H-W retains a decent 48 % conversion and 18 % 5-HMF yield.
20 Moreover, it converts 80 % fructose and yields 50 % 5-HMF after 3 h while the blank test
21 still shows no conversion, further proving the catalytic effect of the sulfonic acid groups
22 present in the UiO-66-SO₃H-W catalyst (Figure S11). Finally, after 6 h of reaction at 80
23 °C, the maximum fructose conversion was 41 % for blank test and 94 % for UiO-66-
24 SO₃H-W with 5-HMF yields of 14 % and 66 %, respectively. Thus, in order to better
25 evaluate a catalyst's performance in fructose dehydration using DMSO as solvent, it is

1 proposed to apply rather mild conditions *i.e.* 80 °C (or less) for a maximum duration of
2 3 h. These conditions would allow to neglect the effect of DMSO and attribute fructose
3 conversion as well as 5-HMF yield to the solid acid catalyst only. For higher
4 temperatures, the 5-HMF yield increased quickly with a maximum reached after 2 h, 30
5 min and 30 min for reactions performed at 100, 120 and 140 °C, respectively (Figure
6 S11).



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

10 As evident from Table S4, most of the published results on fructose dehydration
11 over MOFs used temperatures of 100 °C and above, which indubitably favor the impact
12 of the DMSO solvent over the catalytic conversion of fructose. In this work, we showed
13 the possibility to reach complete fructose conversion at lower catalyst loading (215 mg
14 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-SO₃H
2 reached ~85 % with a 5-HMF yield of ~70 % in 30 min at 120 °C as compared to 100 %
3 and 76 % respectively in this work. This demonstrates a higher fructose conversion over
4 UiO-66-SO₃H-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-SO₃H-
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-SO₃H), presented better results but with a stoichiometric
10 catalyst:fructose ratio [53].

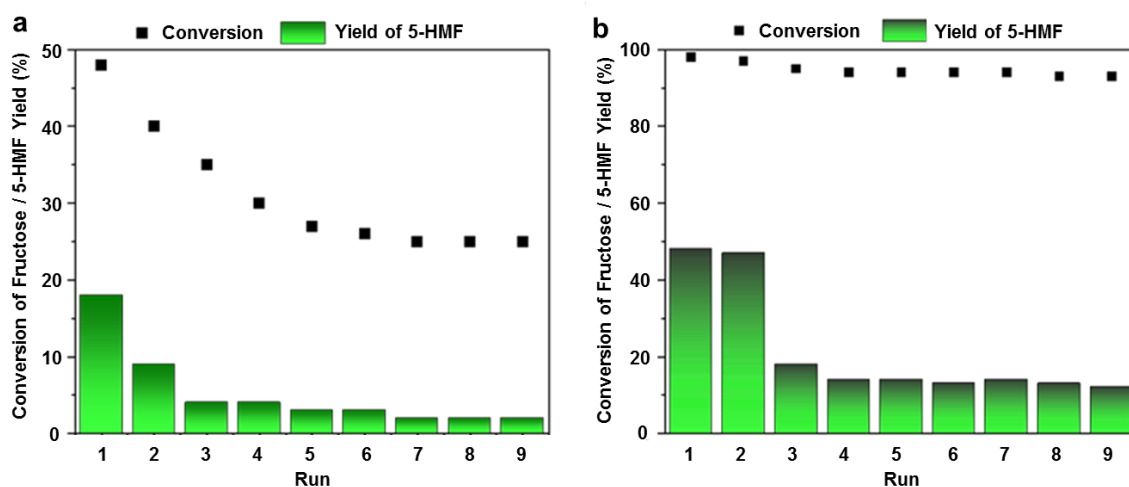
11 Finally, the structural integrity of UiO-66-SO₃H-W, as viewed from XRD patterns
12 in Figure S12, is preserved upon 6 h of catalytic tests up to 120 °C as all diffractograms
13 conserved the ensemble of characteristic reflections of the as-made UiO-66-SO₃H-W.
14 This implies a decent structural stability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

16 **3.2.2. Catalyst recycling**

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

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

1 adsorption of humins on the catalyst, hindering access to the active sites. Herein, their
2 presence is supported by FTIR-ATR analysis on UiO-66-SO₃H-W before and after 9
3 cycles at 80 °C (Figure S13). The spectra demonstrate a new broad band at ~1668 cm⁻¹
4 which corresponds to C=C bond stretching in a furanic ring attributed to humins, while
5 the bands at ~951 and 1004 cm⁻¹ might be indicative of adsorbed 5-HMF species on the
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
8 Figure S14, the mass of the catalyst increased by ~19 % after recycling tests which is
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
12 under ultrasonic irradiation had no effect.



13

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

16 A similar trend is observed upon recycling at 100 °C for 30 min (Figure 8.b).
17 While the selectivity toward 5-HMF dropped significantly after the second run to reach
18 14 % (similar to the blank test), the fructose conversion remains almost quantitative which
19 differs from the blank test. In parallel, the presence of an unknown compound, detected

1 by HPLC and attributed to soluble fructose oligomers [58], increases from the second
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
4 acidity becomes inaccessible due to humins formation. For evaluation of a catalyst's
5 activity in fructose dehydration in DMSO it is critical to consider the solvent effect, which
6 is negligible at 80 °C and becomes considerable at 100 °C and above. Importantly, the
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**

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

19 At 100 °C, it was shown that the UiO-66-SO₃H MOF prepared in DMF reached
20 complete fructose conversion (> 98 %) after 2 h, barely surpassing the activity of the
21 solvent itself, DMSO. On the other hand, the same MOF prepared in water (UiO-66-
22 SO₃H-W) demonstrated complete fructose conversion already after 30 min under the
23 same conditions. This catalyst showed high activity within the whole proposed range of
24 temperatures (80-120 °C). Thus, at mild 80 °C, UiO-66-SO₃H-W demonstrated the decent

1 81 % fructose conversion and 52 % 5-HMF yield after 3 h while the blank test in DMSO
2 showed no fructose conversion.

3 Additionally, UiO-66-SO₃H-W exhibited a well-pronounced structural stability.
4 After 6 h of catalytic tests up to 120 °C, the catalyst retained its crystal structure.
5 Moreover, its structural integrity was proven by performing 9 consecutive catalytic runs
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
9 of the blank tests at 80 °C and 100 °C, respectively. Thus, it was shown that 80 °C is an
10 acceptable temperature to examine a catalyst's activity without the effect of DMSO. On
11 the other hand, frequently reported fructose conversion and 5-HMF yield at 100 °C and
12 above should be attributed to the dual catalyst/DMSO activity.

1 **ASSOCIATED CONTENT**

2 **Supporting Information.** The Supporting Information is available free of charge at DOI:

3 10xxxx/xxxxx.

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

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12

13 **Acknowledgements**

14 The Chevreur Institute is thanked for its help in the development of this work through the
15 ARCHI-CM project supported by the “Ministère de l’Enseignement Supérieur de la
16 Recherche et de l’Innovation”, the region “Hauts-de-France”, the ERDF program of the
17 European Union and the “Métropole Européenne de Lille”. B. Yeskendir is grateful to
18 the Polytechnic University Hauts-de-France and the University of Lille for the PhD
19 funding. M. Trentseaux is acknowledged for the Raman analyses. P.M. de Souza
20 acknowledges the Région Hauts-de-France, I-SITE and MEL for the support in the frame
21 of CatBioInnov and RECABIO projects.

22

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