

Supplementary Materials

Quantification of the Microwave Effect in the Synthesis of 5-Hydroxymethylfurfural over Sulphonated MIL-101(Cr)

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S. Supplementary content

- Section S1 shows the typical microwave pressure and power profile using standard power mode.
- Section S2 addresses the calibration curves and the method used for HPLC analysis and performed calculations.
- Section S3 displays solvents information and the DMSO alignment to the applied electric field of MW.
- Section S4 shows the possible reaction over MIL-101(Cr)-SO₃H.

- Section S5 shows the post-reaction mixture of 5-HMF degradation.
- Section S6 shows an overview of the reported kinetic models on sugar dehydration over heterogeneous catalysts in comparison to this work.

S1. Microwave pressure and power profile

A typical microwave experiment was performed in a heavy-duty pressure stable (max. pressure 20 bar) microwave reactor (10 mL) capped with a PTFE septum. A pre-stirring time of 15 s was set to ensure a homogeneous mixture when the heating was initiated. Irradiation began, and the microwave power was continuously adjusted to give the selected temperature, monitored, and controlled via standard control mode. When the preset temperature was reached, the experiment time was activated and initiated a countdown. When the “safe” temperature was reached, the MW opened to remove the glass reactor. The reactants were separated and filtered to prepare the HPLC sample.

S1.1. Microwave power profile over standard power mode

The microwave power reported in this work refers to the initial microwave power employed to heat the reaction mixture to the preset temperature. After this temperature was reached, the microwave power was varied to keep the reaction at a constant temperature. It was more or less the same for all the reactions, independent of the initial microwave power (Figure S. 1).

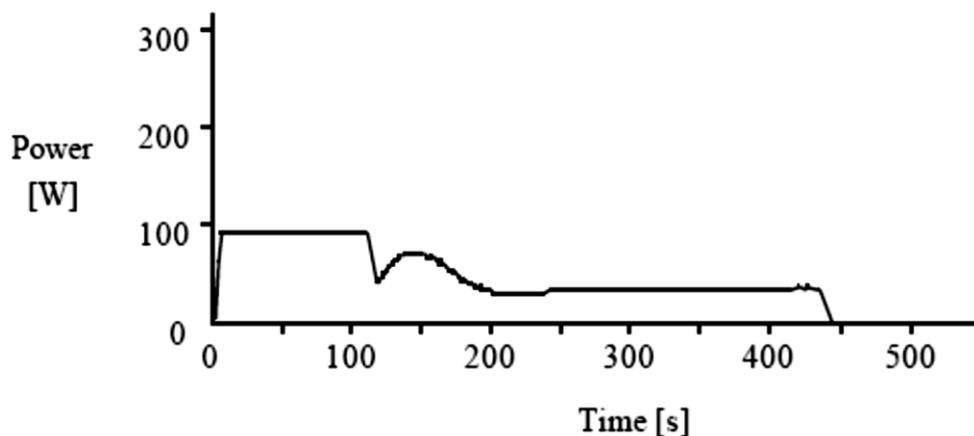


Figure S1. Typical microwave power (W) profile as a function of time (s)

S1.2. The microwave pressure profile

A typical microwave pressure profile as a function of reaction time (s) is displayed below (Figure S.2).

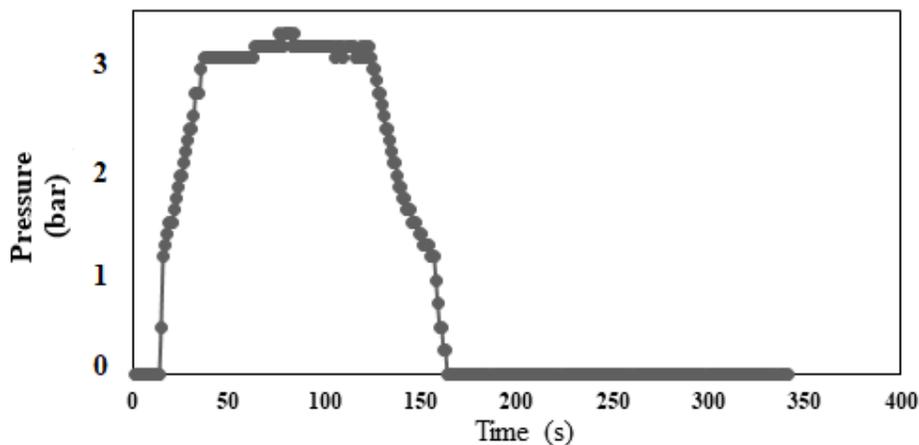


Figure S2. Typical microwave pressure (bar) profile as a function of time (s).

Table S. 1. Heating profile data for fructose dehydration in MW reactor

Heating		Cooling	
Time	T (°C)	Time	T (°C)
0:10	26	0:00:05	159
0:09:55	34	0:00:10	154
0:09:50	48	0:00:15	151
0:09:45	57	0:00:20	148
0:09:40	63	0:00:25	145
0:09:35	74	0:00:30	143
0:09:30	79	0:00:35	141
0:09:25	87	0:00:40	139
0:09:20	94	0:00:45	137
0:09:15	98	0:00:50	135
0:09:10	102	0:00:55	133
0:09:05	107	0:01:00	132
0:09:00	111	0:01:05	130
0:08:55	114	0:01:10	128
0:08:50	118	0:01:15	127
0:08:45	120	0:01:20	125
0:08:40	123	0:01:25	124

0:08:35	126	0:01:30	122
0:08:30	129	0:01:35	122
0:08:25	131	0:01:40	120
0:08:20	133	0:01:45	119
0:08:15	135	0:01:50	118
0:08:10	137	0:01:55	117
0:08:05	140	0:02:00	116
0:08:00	142	0:02:05	114
0:07:55	144	0:02:10	113
0:07:50	146	0:02:15	112
0:07:45	148	0:02:20	111
0:07:40	149	0:02:25	110
0:07:35	151	0:02:30	109
0:07:30	153	0:02:35	109
0:07:25	154	0:02:40	107
0:07:20	156	0:02:45	107
0:07:15	157	0:02:50	105
0:07:10	158	0:02:55	105
0:07:05	158	0:03:00	104
0:07:00	158	0:03:05	103
0:06:55	158	0:03:10	102
0:06:50	158	0:03:15	101
0:06:45	158	0:03:20	101
0:06:40	158	0:03:25	100
0:06:35	158	0:03:30	99
0:06:30	158	0:03:35	98
0:06:25	158	0:03:40	98
0:06:20	158	0:03:45	97
0:06:15	158	0:03:50	96
0:06:10	158	0:03:55	95
0:06:05	158	0:04:00	94
0:06:00	158	0:04:05	94
0:05:55	158	0:04:10	93
0:05:50	158	0:04:15	93
0:05:45	158	0:04:20	92
0:05:40	158	0:04:25	91
0:05:35	158	0:04:30	91
0:05:30	158	0:04:35	90
0:05:25	158	0:04:40	89
0:05:20	158	0:04:45	89

0:05:15	158	0:04:50	88
0:05:10	158	0:04:55	87
0:05:05	158	0:05:00	87
0:05:00	159	0:05:05	86
0:04:55	160	0:05:10	86
0:04:50	160	0:05:15	85
0:04:45	161	0:05:20	84
0:04:40	160	0:05:25	84
0:04:35	161	0:05:30	83
0:04:30	160	0:05:35	83
0:04:25	160	0:05:40	82
0:04:20	160	0:05:45	82
0:04:15	160	0:05:50	81
0:04:10	162	0:05:55	80
0:04:05	160	0:06:00	80
0:04:00	161	0:06:05	80
0:03:55	160	0:06:10	79
0:03:50	161	0:06:15	79
0:03:45	161	0:06:20	78
0:03:40	161	0:06:25	78
0:03:35	162	0:06:30	77
0:03:30	160	0:06:35	76
0:03:25	161	0:06:40	76
0:03:20	160	0:06:45	76
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0:02:20	160	0:07:45	70
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0:02:10	160	0:07:55	70
0:02:05	161	0:08:00	69
0:02:00	160	0:08:05	69

0:01:55	160	0:08:10	68
0:01:50	160	0:08:15	68
0:01:45	160	0:08:20	68
0:01:40	161	0:08:25	67
0:01:35	160	0:08:30	67
0:01:30	161	0:08:35	66
0:01:25	160	0:08:40	66
0:01:20	160	0:08:45	66
0:01:15	161	0:08:50	65
0:01:10	160	0:08:55	65
0:01:05	160	0:09:00	65
0:01:00	160	0:09:05	64
0:00:55	161	0:09:10	64
0:00:50	160	0:09:15	64
0:00:45	160	0:09:20	63
0:00:40	160	0:09:25	63
0:00:35	160	0:09:30	63
0:00:30	160	0:09:35	63
0:00:25	160	0:09:40	62
0:00:20	160	0:09:45	61
0:00:15	160	0:09:50	61
0:00:10	161	0:09:55	61
0:00:05	160	0:10:00	61
0:00:00	160	0:10:05	61
0:00:05	159	0:10:10	60

S2. Calibration curve and HPLC calculations

High-performance liquid chromatography (HPLC, Agilent 1200) equipped with Aminex HPX-87H ion-exclusion column (7.8 × 300 mm, Bio-Rad) and a refractive index (in the range of 1.00 to 1.75 refractive index unit) detector was used for the quantification of 5-HMF. The samples were diluted, filled in 1.5 mL screw neck vials, and then placed in HPLC trays. The samples were injected with a volume of 20 µL. HPLC water containing 0.005M of H₂SO₄ was used as a mobile phase at a flow rate of 0.6 mL·min⁻¹. The column temperature was set at 60 °C and the refractive index detector at 45 °C. Figure S.3 is the

HPLC chromatogram of fructose, formic acid (FA), levulinic acid (LA), and 5-HMF at the retention time of 10.03, 14.10, 17.02, and 37.35 min, respectively.

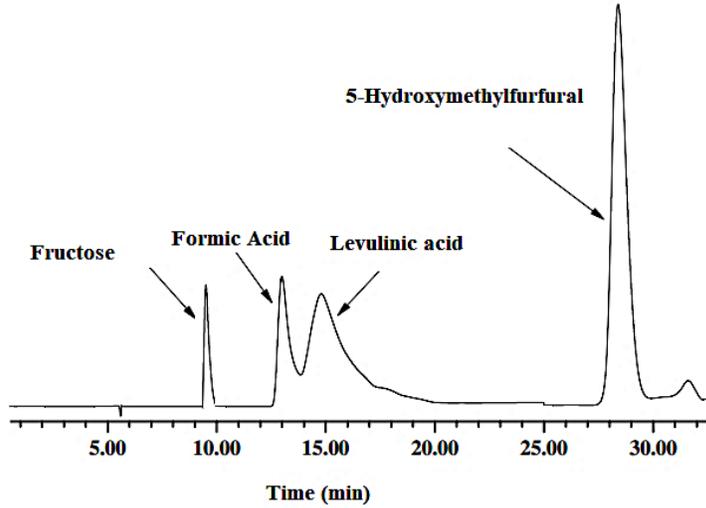


Figure S3. HPLC chromatogram of fructose, FA, LA, and 5-HMF.

Standard calibration curves were made from pure fructose, FA, LA, and 5-HMF with concentrations of 20, 40, 60, 80, and 100 mg·L⁻¹. The corresponding calibration curves can be found in Figure S.4. The data from the calibration curves were taken into account to calculate the yield and selectivity of HMF and fructose conversion at the end.

The calculation begins with the initial concentration of fructose by Eq. (S-1) in the reaction vessel, where 100 mg of fructose (with a molecular mass of 180.16 g·mol⁻¹) was dissolved in 3 mL of solvent.

$$C_{\text{fructose initial}} \left[\frac{\text{mg}}{\text{L}} \right] = \frac{\text{mass}_{\text{fructose initial}}}{\text{volume of solvent}} \quad (\text{S-1})$$

Samples must be diluted before the HPLC analysis. In that regard, an appropriate dilution factor (DF) is figured out by Eqs. (S-2)-(S-3):

$$C_{\text{initial}} \times V_{\text{initial}} = C_{\text{diluted}} \times V_{\text{diluted}} \quad (\text{S-2})$$

$$V_{\text{initial}}[\text{mL}] = \frac{C_{\text{diluted}} \times V_{\text{diluted}}}{C_{\text{original}}} \quad (\text{S-3})$$

For targeting diluted samples to be $C_{\text{diluted}} = 100 \text{ mg}\cdot\text{L}^{-1}$ and $V_{\text{diluted}} = 5$, Eq. (S-3) gives V_{initial} to be 0.015 mL with initial fructose concentration of 33,333 mg·L⁻¹.

Then, from Eq. (S-4), a DF of 333 is obtained.

$$\mathbf{Dilution\ factor} = \frac{V_{\text{diluted}}}{V_{\text{initial}}} \quad (\text{S-4})$$

Via the areas of fructose and HMF acquired from HPLC, the diluted concentration can be figured out by Eq. (S-5) and Eq. (S-6):

$$C_{\text{diluted fructose}} \left[\frac{\text{mg}}{\text{L}} \right] = \frac{\text{Fructose area under HPLC spectra}}{\text{Slope of fructose calibration curve}} \quad (\text{S-5})$$

$$C_{\text{diluted HMF}} \left[\frac{\text{mg}}{\text{L}} \right] = \frac{\text{HMF area under HPLC spectra}}{\text{Slope of HMF calibration curve}} \quad (\text{S-6})$$

Since the initial concentrations of each compound of interest must be multiplied by the DF, Eq. (S-7) and Eq. (S-8):

$$C_{\text{fructose}} \left[\frac{\text{mg}}{\text{L}} \right] = C_{\text{diluted fructose}} \times \mathbf{Dilution\ factor} \quad (\text{S-7})$$

$$C_{\text{HMF}} \left[\frac{\text{mg}}{\text{L}} \right] = C_{\text{diluted 5-HMF}} \times \mathbf{Dilution\ factor} \quad (\text{S-8})$$

Furthermore, concentration could be converted into molarity, followed by moles of unreacted fructose, as the HPLC detected it.

$$M_{\text{fructose}} \left[\frac{\text{mmol}}{\text{L}} \right] = \frac{C_{\text{fructose}}}{Mm_{\text{fructose}}} \quad (\text{S-9})$$

$$M_{\text{HMF}} \left[\frac{\text{mmol}}{\text{L}} \right] = \frac{C_{\text{HMF}}}{Mm_{\text{HMF}}} \quad (\text{S-10})$$

$$n_{\text{fructose unreacted}} [\text{mmol}] = M_{\text{fructose}} \times V_{\text{initial}} \quad (\text{S-11})$$

Knowing the initial moles of fructose (Eq. 12), the reacted number of moles of fructose and produced 5-HMF moles can be calculated by Eq. (S-13) and Eq. (S-14), respectively:

$$n_{\text{fructose initial}} [\text{mmol}] = \frac{\text{mass}}{\text{molecular mass}} \quad (\text{S-12})$$

$$n_{\text{fructose reacted}} [\text{mmol}] = n_{\text{fructose initial}} - n_{\text{fructose unreacted}} \quad (\text{S-13})$$

$$n_{\text{5-HMF produced}} [\text{mmol}] = M_{\text{5-HMF}} \times V_{\text{initial}} \quad (\text{S-14})$$

By plugging in the appropriate values from the equations above, the final results – yield and selectivity of 5-HMF and fructose conversion are obtained by Eqs. (S-15)-(S-17):

$$\mathbf{5 - HMF\ yield\ [\%]} = \left(\frac{\mathbf{moles\ of\ 5-HMF\ produced}}{\mathbf{initial\ moles\ of\ fructose}} \right) \times \mathbf{100} \quad (\text{S-15})$$

$$\mathbf{HMF\ selectivity\ [\%]} = \left(\frac{\mathbf{moles\ of\ HMF\ produced}}{\mathbf{converted\ moles\ of\ fructose}} \right) \times \mathbf{100} \quad (\text{S-16})$$

$$\mathbf{Fructose\ conversion\ [\%]} = \left(\frac{\mathbf{converted\ moles\ of\ fructose}}{\mathbf{Initial\ moles\ of\ fructose}} \right) \times \mathbf{100} \quad (\text{S-17})$$

The yields of FA and LA are calculated in an analogous procedure with fructose and 5-HMF using calibration in Figure S.4

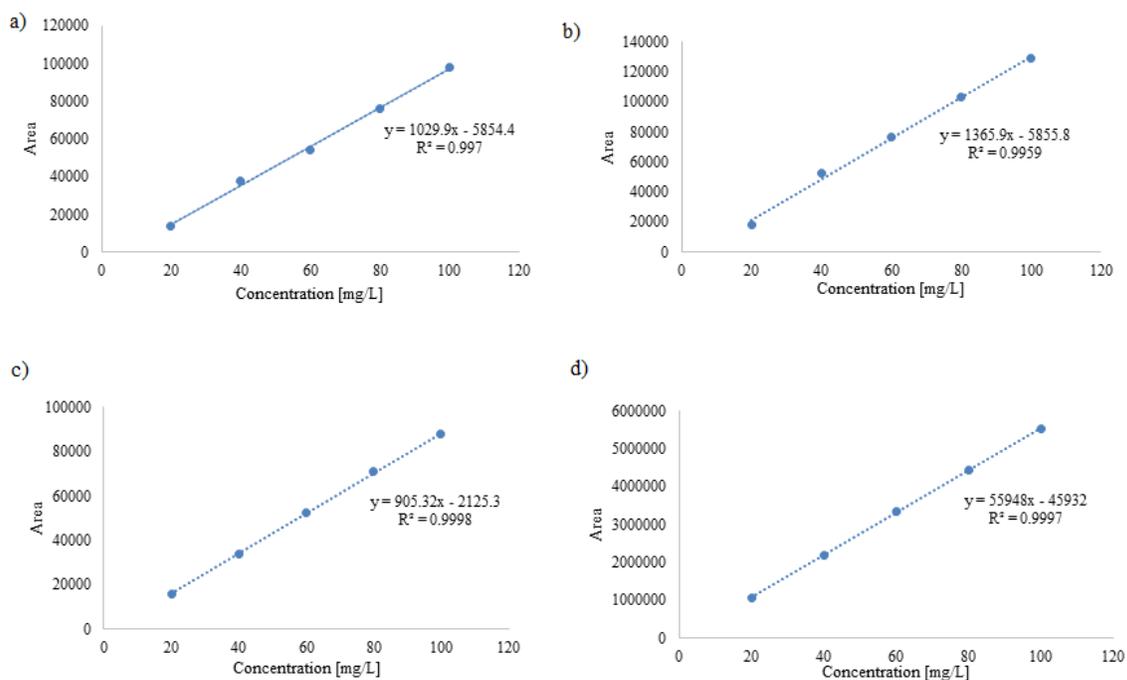


Figure S.4. HPLC calibration curve of (a) fructose, (b) FA, (c) LA, and (d) 5-HMF.

S3. DMSO and Acetone

The dipole-dipole type interaction between the dipolar solvent and polar reactants can produce electrostatic polar effects; Figure S.5 shows the DMSO alignment to the applied electric field by rotation.

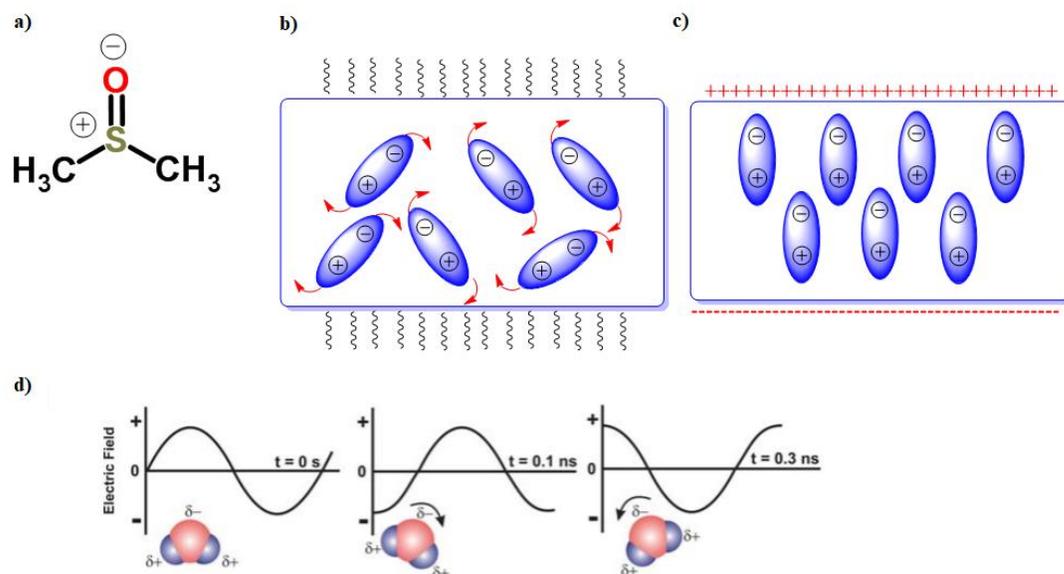


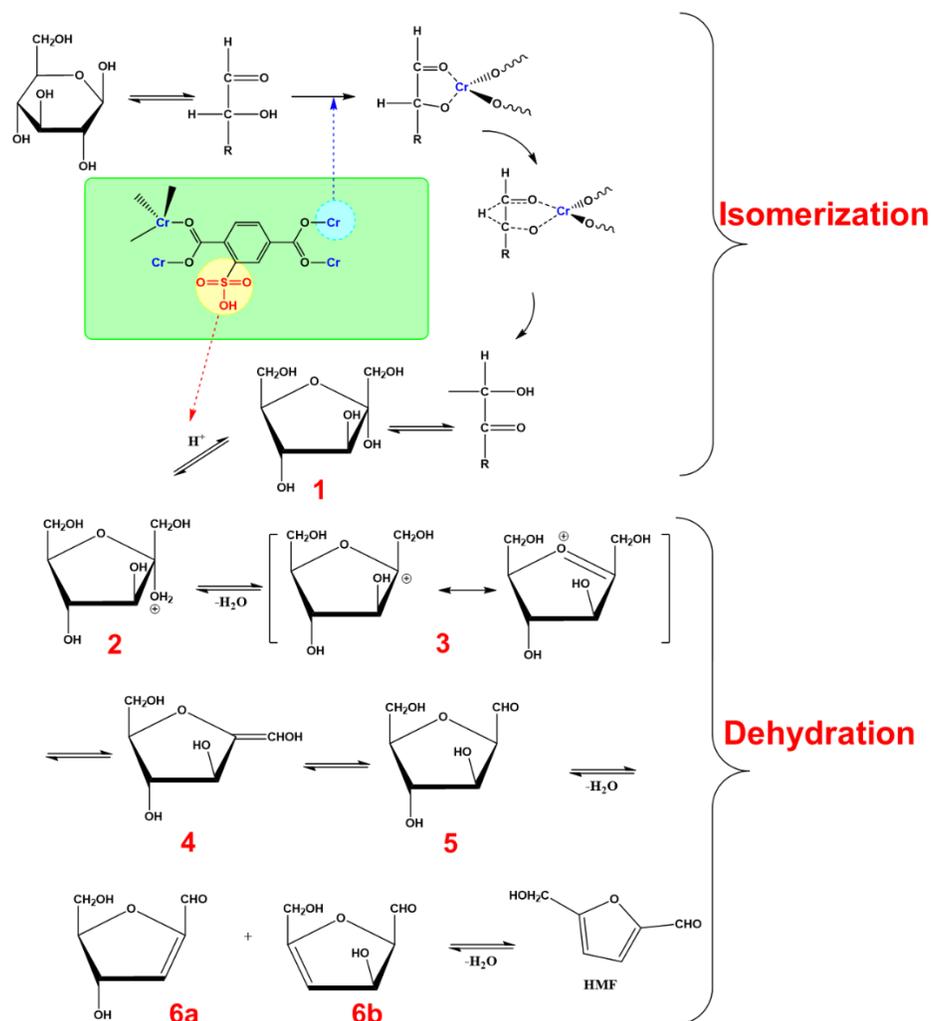
Figure S5. Representation of (a) DMSO molecule, (b) thermal microwave effect where the induced microwave-irradiation-molecules disperses heat and the dipole-dipole interaction of the DMSO start, (c) alignment of the dipoles of the DMSO and charges of the electric field, and (d) DMSO molecule alignment to the applied electric field by rotation.

S4. Possible reaction over MIL-101(Cr)-SO₃H

It was reported that two-thirds of sulfo groups dangling on the sulphonated MIL-101(Cr) products are in the Brønsted acid form that can easily release protons for catalysis application [1]. Thus, MIL-101(Cr)-SO₃H possesses strong acid sites; hence, fructose dehydration is likely to occur through the E1 elimination reaction via the carboxylic group of the parent MOF or sulpho group for the sulphonated MOF [2,3].

The transformation reaction mechanism of fructose to 5-HMF over the bifunctional sulfonated MIL-101 (Cr) was understood to involve a binding domain for the reactant and catalytic domain. It is assumed that the hydride shift will be facilitated by the Cr^{+3} ion and the reaction by the $-\text{SO}_3\text{H}$ group, which acts as Brønsted acid to eliminate water molecules. Scheme S.1 the dehydration reaction occurring in the following steps:

1. In the first step, fructose 1, which exists in its furanose form, is protonated in the C-2-OH position.
2. From the formed C-2-OH₂ moiety 2, water, as a good leaving group, is released.
3. Thereby, the first condensation step is accomplished, resulting in the formation of a fructofuranosyl cation 3.
4. In the following deprotonation, an enol intermediate 4 is generated, which is in equilibrium with the corresponding keto form 5.
5. Subsequently, a second molecule of water can be eliminated either from the C-3-OH or C-4-OH position resulting in the formation of 6a or 6b, respectively.
6. Finally, the last dehydration step, which is the only irreversible step in the mechanism, delivers HMF.



Scheme S. 1. Proposed mechanism of glucose isomerization followed by fructose dehydration to 5-HMF over bifunctional MOF, MIL-101 SO₃H

S5. Post-reaction mixture of 5-HMF degradation

At both MW and CH conditions, as the catalyst-to-substrate ratio and temperature increased, the color of the solution became gradually darker because side reactions forming humins and polymers were enhanced. It was also noted that the intensity of the colouration increased with the initial concentration of fructose, see Figure S.6. This is attributed to polymerization of 5-HMF with the unreacted fructose. Figure S.6 indicates the remarkable

phenomenon observed at higher temperatures and longer reaction times in which the mixture gradually changed from orange color to dark brown dense liquid. It was also noticed that some humins are partially soluble in DMSO/Acetone.

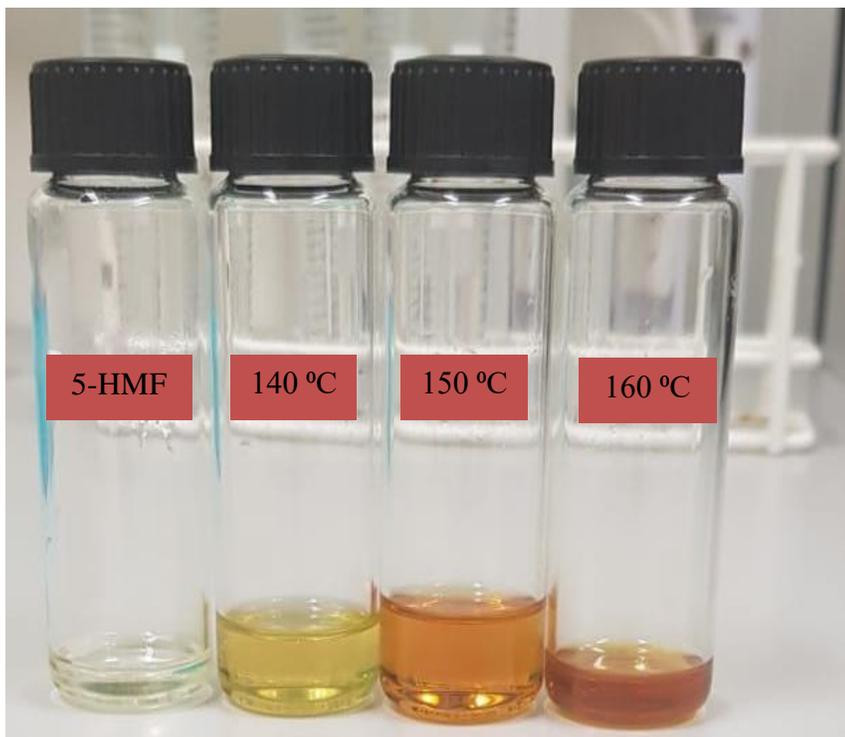


Figure S1. Post reaction mixture of fructose dehydration. The colour variation shows the 5-HMF degradation at higher reaction temperature ($\sim 99\%$ conversion) in DMSO/acetone, 10 mg catalyst.

S6. Comparison with similar studies over heterogeneous catalysts

Table S2. Overview of the reported kinetic models on sugar dehydration over heterogeneous catalysts compared to this work.

Entry	Feed	Reaction network	T (°C) / Reactor	Solvent	Catalyst	Reaction order	Activation energy (kJ/mol)	Ref.
1	Fructose (0.03 wt%)	$\text{Fru} \xrightarrow{1} \text{I} \xrightarrow{2} \text{HMF} \xrightarrow{3} \text{LA} + \text{FA}$ $\text{I} \xrightarrow{4} \text{Humins}$	140-160, CH	DMSO/Ac	MIL-101-SO ₃ H	1 st order	$E_1 = 88 \pm 33$ $E_2 = 103 \pm 43$ $E_3 = 87 \pm 45$	This work
2	Fructose (0.03 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF} \xrightarrow{2} \text{LA} + \text{FA}$ $\text{HMF} \xrightarrow{3} \text{Humins}$	140-160, CH	DMSO/Ac	MIL-101-SO ₃ H	1 st order	$E_1 = 38 \pm 17$ $E_2 = 99 \pm 24$	This work
3	Fructose (0.03 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF}$	140-160, CH	DMSO/Ac	MIL-101-SO ₃ H	1 st order	$E_1 = 48 \pm 2$	This work
4	Fructose (0.1 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF}$	120-150, CH	DMSO	MIL-101-SO ₃ H	1 st order	$E = 55 \pm 5$	[2]
5	Fructose (2 wt%)	$\text{Fru} \xrightarrow{1} \text{I} \xrightarrow{2} \text{HMF} \xrightarrow{3} \text{LA} + \text{FA}$ $\text{I} \xrightarrow{4} \text{Humins}$	125-145, CH	H ₂ O	ZrPO-700	1 st order	$E_1 = 186$ $E_2 = 209$ $E_3 = 24$ $E_4 = 91$	[4]

6	Fructose (2 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF}$	120-150, MW	DMSO/ H ₂ O	Strong acidic cation- exchange resin	1 st order	$E = 161$	[5]
7	Fructose (2 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF}$	120-150, MW	DMSO/Ac	Strong acidic cation- exchange resin	1 st order	$E = 60$	[5]
8	Fructose (0.1 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF} \xrightarrow{2} \text{LA} + \text{FA}$	160-178, CH	H ₂ O/MIBK	H mordenites	1 st order	$E_1 = 141$ $E_2 = 64$	[6]
9	Fructose (0.01 wt%)	$\text{Fru} \xrightarrow{1} \text{HMF}$	100-120, CH	DMSO	SBA-15-SO ₃ H	1 st order	$E_1 = 56$	[5]

S7. The effect of the initial fructose concentration on 5-HMF selectivity

Table S3. Substrate mass effect on 5-HMF yield and selectivity over MIL-101(Cr)-SO₃H(3).

Reaction conditions: MWcondition, 3mL DMSO/acetone (70:30) and at 5 min.

Temp (°C)	Substrate [mg]	Fructose conversion [%]	5-HMF yield [%]	5-HMF selectivity [%]
160	100	99	61	62
	300	99	61	61
	800	99	61	61
170	100	98	54	55
	300	99	54	54
	800	99	55	55

References

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