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Sulfonic acid-functionalised zeolites for fructose dehydration into 5-hydroxymethylfurfural

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Abstract

Biomass-derived 5-hydroxymethylfurfural (HMF) is a versatile and key platform chemical critical to underpinning a sustainable chemical industry based on biomass. This study explores the innovative use of zeolites and hierarchical zeolites, derived through alkaline desilication, as catalytic materials for fructose dehydration. Functionalised with sulfonic acid sites, these materials demonstrate elevated catalytic performance, particularly maximising HMF yields. The increased mesoporosity facilitates higher sulfonic acid incorporation, leading to improved fructose conversion. However, yields are sensitive to reaction duration, with longer time negatively impacting the selectivity towards HMF due to further in-series reactions. Optimal results were achieved under microwave irradiation in a biphasic medium, achieving an HMF selectivity of \sim 73% at fructose conversion of \sim 88% in just 5 min at 170 °C, emphasising energy efficiency and catalyst accessibility. The best catalyst modifications lead to a reduction in the activation energy of fructose conversion by approximately 35% relative to the uncatalysed process, in conjunction with significant improvements in process sustainability, which align with the United Nations sustainable development goals (SDGs) in Affordable and Clean Energy (SDG 7), Industry, Innovation, and Infrastructure (SDG 9), Responsible Consumption and Production (SDG 12), and Climate Action (SDG 13).

1. Introduction

The continuous unsustainable consumption of non-renewable fossil resources, coupled with growing concerns about the severity of anthropogenic environmental pollution, motivates the development and implementation of sustainable processes within the chemical industry [1, 2]. Biomass conversion into value-added chemicals has emerged as a desirable and viable alternative for reducing humanity's dependence on fossil resources [2–4]. Among the plethora of possible bio-based chemicals, 5-hydroxymethylfurfural



(HMF) is considered a prime candidate, given its potential as a key intermediate in the production of replacements for crude oil based fuels, solvents, and monomers [2–4]. HMF production via carbohydrate dehydration, specifically acid-catalysed fructose dehydration, represents a convenient and practical production route [5–8].

Various acid catalysts, both homogenous (e.g. mineral [9] and organic acids [10]) and heterogeneous, have been investigated for fructose dehydration to HMF. Considering separation efficiency, heterogeneous catalysts are preferred, with HMF production from fructose reported over H-form zeolites [11, 12], ion-exchange resins [13], and supported sulfonic acids [14]. The inherent Brønsted acidity of such systems governs dehydration reactions [12, 15, 16], of which catalysts with sulfonic acid groups (-SO₃H) show high efficiency due to their strong acidity [5–8, 14, 17, 18]. Conventional deposition of sulfonic acids onto support structures proceeds through the grafting of mercaptopropyl silanes, typically in hydrocarbon solvents, e.g. toluene [5, 18–22]. However, to prevent the undesired use of solvents with an unfavourable environmental, health and sustainability profile within catalysts synthesis [23], it is desirable to employ 'greener' solvents, with water being the best example [24].

Among the array of support materials, zeolites are interesting candidates due to their high surface area, good thermal stability, and commercial availability and economics [19, 20, 25, 26], which lend them to applications in various fields such as ion exchange [27–29], gas separation [29, 30], and catalysis [29, 31]. However, their microporous nature imposes substantial diffusion resistance, limiting both incorporating and converting bulky species and substrates. Hierarchical zeolites with the typical micro-meso-porous networks [32] can overcome this through the provision of secondary large pores, allowing higher molecular transfer within their zeolitic frameworks. In addition, the presence of reactive terminal silanols on the surface of mesopores can serve as the anchoring point as well for functionalisation via silanisation reactions [33].

A major drawback that plagues HMF production is the occurrence of undesirable side reactions (scheme 1) [16, 34, 35], which are exacerbated when conducted in water, resulting in the formation of soluble and insoluble humins, and formic and levulinic acid, with HMF yields typically under 50% [15, 35]. Employing alternative reaction media, including polar organic solvents [5, 6, 36–39], and ionic liquids [7, 40], was found to promote higher HMF yields. For example, DMSO [5, 17], and ionic liquids (e.g. [bmim]Br [40] and [bmim]Cl [7]) can achieve yields in excess of 90% and 80%, respectively. However, their high boiling points hinder subsequent downstream product isolation [15, 41], while the catalytic nature of the former masks the intrinsic performance of added catalysts [12], and economic concerns plague the latter [42]. Alternatively, interactions of the product with the catalytic active sites, which lead to unwanted side reactions, can be controlled to maximise HMF yields, either through diffusion [14] or the deployment of biphasic reaction systems [12]. The latter combines an aqueous reaction phase (which contains the catalysts) and a second immiscible extraction phase (often an organic solvent), allowing HMF extraction as it is produced, thereby reducing undesirable production of humins and/or HMF hydration to levulinic and formic acid [43, 44]. Employing lower boiling point organic solvents as the extraction phase, i.e. methyl isobutyl ketone (MIBK) and 2-butanol (2-BuOH), can aid product isolation, with both (alongside water) ideal green reaction media candidates [45, 46].

This work aimed to develop novel solid acid catalysts of sulfonic acid functionalised zeolites for facile fructose dehydration into HMF, with the aim of enhancing the performance of industrially relevant catalytic materials. We first explored various commercial zeolites (i.e. HY, HBeta, HZSM5 and HMOR) and sulfonic

acid-functionalised derivatives in a biphasic reaction medium comprising H_2O (reaction phase) and MIBK and 2-BuOH (extraction phase), identifying HY as a candidate (due to its superior performance and green credentials on initial screening) for further engineering. To control porosity, the parent zeolites were subjected to alkaline treatments, while acidity was tuned via functionalisation with the sulfonic acid groups. In addition, modification of the process reaction parameters was investigated to understand their impact. From these, the optimal process conditions and catalyst choice are established based on those resulting in the greatest energy efficiency and greenest credentials.

2. Experimental section

2.1. Materials and chemicals

D(-)-fructose (for biochemistry), D-(+)-glucose (≥99.5%), levulinic acid (98%), formic acid (for HPLC), HMF (99.9%), furfural (ACS reagent, 99%), toluene (HPLC grade), hydrogen peroxide (H₂O₂, 50 wt %), isopropyl alcohol (IPA, HPLC grade), (MIBK, ACS reagent, ≥99.9%), 2-butanol (anhydrous, 99.5%), sodium hydroxide (NaOH, 99%), ammonium nitrate (NH₄NO₃, ACS reagent, ≥98%), potassium chloride (KCl) were purchased from Sigma Aldrich. 3-mercaptopropyltrimethoxysilane (MPTMS, 97%) was purchased from Fluorochem Limited. All the chemicals were used as received without further purification. HY (CBV760), NH₄-ZSM5 (CBV5524G), NH₄-Beta (CP814C), and NH₄-MOR (CBV21A) were purchased from Zeolyst International (UK). HY (CBV760) is manufactured via steam and acid treatment of a high Si:Al HY zeolite, which, upon tuning Si:Al, results in the creation of complementary mesoporosity [47]. Before use, NH₄-ZSM5, NH₄-Beta, and NH₄-MOR were calcined at 550 °C for 5 h (ramp rate 5 °C min⁻¹) to convert to the H⁺ form denoted as HZSM5, HBeta, and HMOR, respectively.

2.2. Catalyst preparation

2.2.1. Alkaline treatment

Parent HY zeolite (5 g) was dispersed in aq. NaOH (various concentrations of 0.001, 0.01, 0.055 and 0.1 M, 100 cm³). The slurry was heated to 50 °C and stirred for 2 h, then quenched using an ice water bath for 15 min and centrifuged (3000 G, 10 min) to isolate the solid. The solid was washed five times with deionised (DI) water before being dried under vacuum at 120 °C overnight. Ion exchange was conducted with aq. NH₄NO₃ (1 M, 30 cm³ g_{zeolite}⁻¹) in triplicate at 80 °C for 2 h under stirring. The solid was isolated by centrifugation, washed five times using DI water, and dried at 120 °C under vacuum overnight. The solid was calcined at 550 °C for 5 h (ramp rate 5 °C min⁻¹) to give the H⁺ form zeolite. The obtained samples were denoted as HY, HY-0.001, HY-0.01, HY-0.055, and HY-0.1, respectively, in accordance with the concentrations of NaOH used during desilication.

2.2.2. Grafting sulfonic groups in toluene/ H_2O

Scheme 2 summarises the synthesis route of sulfonic-acid functionalised zeolites. Parent HY, HZSM5, HBeta, or HMOR zeolite (1 g), and MPTMS (2.5 g) were dispersed in toluene (20 cm³). The solution was heated to 60 °C and stirred for 6 h, before quenching in an ice water bath for 15 min and centrifugation (3000 G, 10 mins) to obtain the solid product. The solid was washed five times with ethanol before being dried at 100 °C overnight. Subsequently, thiol groups were converted into sulfonic acid groups by oxidation through stirring in an aq. H_2O_2 solution (50 wt.%, 1/10 (wt./vol.) catalyst/ H_2O_2) at room temperature for at least 10 h. The solid was isolated by centrifugation (3000 G, 10 mins) and washed five times with ethanol before being dried at 100 °C overnight. The obtained samples were denoted as SO_3H/HY -Tol, $SO_3H/HZSM5$ -Tol, $SO_3H/HBeta$ -Tol, $SO_3H/HMOR$ -Tol, respectively. Aqueous grafting was conducted for HY zeolites under an identical protocol, except for the substitution of toluene with DI H_2O as the grafting solvent. The obtained catalyst was named SO_3H/HY - H_2O . The use of hierarchical HY (alkane treated) as support architectures yielded SO_3H/HY -0.001- H_2O , SO_3H/HY -0.01- H_2O , SO_3H/HY -0.055- H_2O and SO_3H/HY -0.1- H_2O , respectively (with the numerical value representing the concentration employed during desilication).

2.3. Catalyst characterisation

X-ray diffraction (XRD) patterns were obtained using the Philips X'Pert x-ray diffractometer, employing a CuK α radiation source ($\lambda = 1.5406$ Å) operating at 40 kV and 40 mA, with scans collected from 5° to 55° 2 θ with a step size of 0.0334°. Relative crystallinity was calculated based on integrated peak areas [48, 49], with the parent zeolite as the [48]. Nitrogen (N₂) adsorption analysis was carried out at liquid N₂ temperature of -196 °C on a Quantachrome Quadrasorb SI-20. Prior to analysis, samples were degassed using a Flovac Degasser FVD-3 Quantachrome instrument at 250 °C for 12 h. The specific surface area of materials was determined using the Brunauer–Emmett–Teller (BET) method over the relative pressure range from 0.05 to



0.2, where a linear relationship was observed. Pore size analysis was conducted using the Barrett-Joyner–Halenda method and the desorption branch of isotherms. Scanning electron microscopy (SEM) was performed using Philips XL30 FEG, operating with a beam acceleration voltage of 15 kV. Particle size distribution was analysed using Image-J[®] software. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis SUPRA, equipped with a monochromated Al k α (1486.69 eV) x-ray source operating at 15 mA emission and 12 kV HT (180 W) with a spot size/analysis area of 700 \times 300 μ m. Spectra were processed and deconvoluted using a CasaXPS v. 2.3.19PR1.0. Background subtraction was performed using the shirley or quadratic method. Binding energies were calibrated to adventitious carbon at 284.8 eV. CHNS analysis was performed on a Thermo Scientific Flash 2000 Elemental Analyser. Brønsted acidity of the catalyst was determined by ion exchange and pH measurement with a Jenway PH meter [50]. Catalyst (0.1 g) was mixed with aq. KCl (0.1 M, 10 cm³) and stirred for 24 h at room temperature. pH evolution was measured for each mixture until a constant value was recorded. The concentration of accessible acid groups was calculated using equation (S1) [50] in the supporting information (SI). Pyridine adsorption on acid sites was evaluated by Fourier transform infrared (FTIR) spectroscopy, conducted using a Bruker Tensor-27 FTIR spectrometer. The ground sample (sieved to \geq 300 mesh) was dried at 140 °C for 12 h prior to pyridine (15 ml pyridine) vapour exposure in a vacuum desiccator at -0.1 MPa for 12 h. Following adsorption, the liquid pyridine was removed from the desiccator, and the sample was maintained at -0.1 MPa for 30 min. The sample was dried at 140 °C for 12 h to remove any physisorbed pyridine. The sample was pressed into a mould to provide a smooth surface for analysis.

2.4. Catalysis

Fructose dehydration was conducted in an Anton Paar Monowave 400 reactor using 30 cm³ reaction vials (Anton Paar G30). Fructose (0.15 g, 5 wt./v%) was dissolved in the reaction phase DI H₂O (3 cm³) before the catalyst (0.06 g, 2 wt./v%) and extraction phase (6 cm³) of MIBK: 2-BuOH (v/v = 7:3) were added, with the latter having been observed to enhance extraction efficiency in our previous work [12]. The biphasic reaction mixture was heated to 160 °C (160 °C min⁻¹) and held for the desired reaction time with stirring at 800 rpm. The reactor vessel was cooled to 70 °C under flowing air before quenching to room temperature in an ice water bath. The catalyst was isolated by centrifugation (3000 G, 10 min), with aliquots (0.2 cm³) of the reaction and extraction phases prepared for high-performance liquid chromatography (HPLC) analysis by dilution with DI H₂O (1:50 v/v) or IPA (1:50 v/v), and filtration with a polyethersulfone syringe filter (0.2 μ m). Catalyst reusability was evaluated over 4 recycles under optimal conditions, with a constant catalyst:solvent:substrate. For each recycle, the spent catalyst from the previous reaction was recovered via centrifugation (3000 G, 10 min), washed with DI water or acetone (30 cm³) in triplicate, and dried at 80 °C under vacuum overnight. An oxidation regeneration through stirring in an H₂O₂ solution (50 wt.%, 10 cm³) for 24 h was also investigated.

Quantitative analysis of reaction samples was carried out using HPLC on an Agilent Infinity 1220 equipped with refractive index and UV detectors, the latter set at a wavelength of 254 nm. Product resolution was achieved on a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm \times 7.8 mm), using a 0.01 N H₂SO₄ mobile phase (flow rate of 0.6 cm³ min⁻¹) under isothermal conditions (column oven at 50 °C). Humins are calculated from the missing carbon balance. Fructose conversion (mol%), product yield (mol%), product selectivity (%), and the partition ratio (PR) of HMF are defined in the ESI (equations (S2)–(S5)). PR is defined as the ratio of the weight fraction of HMF in the extraction phase to the weight fraction of HMF in the reaction phase [51]. Total energy efficiency coefficient (η) was calculated (equation (S6)), which is the amount of HMF produced per unit of work [12, 17], with total energy consumption evaluated using an inline plug-in power meter to record total energy consumption. Turnover frequency (**TOF**) was calculated via equation (S7). Green metrics, including E-factor (solvent recycled) (equation (S8)), process mass intensity (PMI) (equation (S9)), energy economy coefficient (ε) (equation (S10)), and

environmental energy impact factor (ξ) (equation (S11)), have been calculated to evaluate process efficiency as a way to assess environmental impact [52–55]. Details of the green metrics are presented in the ESI.

Based on the literature [56–58], a pseudo-first-order kinetic model was devised to demonstrate the conversion of fructose. Thus, the rate of fructose conversion is expressed as follows as a first-order reaction:

$$-r[\text{fructose}] = -\frac{-d[\text{fructose}]}{dt} = k[\text{fructose}]$$
(1)

k is the pseudo-first-order rate constant of fructose conversion at a certain reaction temperature (\min^{-1}) , from which activation energies are determined using the Arrhenius equation.

3. Results and discussion

3.1. Catalyst characterisation

XRD patterns of the zeolite supports are consistent with data from the International Zeolite Association, with sulfonic acid grafting shown to have no detrimental impact (as illustrated in figure 1) [59]. HBeta, HZSM5, and HMOR show complete retention of zeolite crystallinity (table 1), with only a slight decrease observed for HY. This apparent decrease in HY coincides with significantly higher sulfur content, which is attributed to its higher surface area, specifically its higher external surface area within this zeolite, which provides additional highly accessible sites for sulfonic acid functionalisation. It is worthwhile noting that this external surface area reflects the combination of mesopores, macropores, and external surfaces. Alkaline treatment of HY, whose effect on XRD patterns is shown in figure S1, reveals a direct correlation in the loss of crystallinity with NaOH solution concentration, with relative crystallinity quantified in table 1. This treatment induces the hydrolysis of Si-O-Al bonds, leading to the creation of Si-OH and Al-OH species, resulting in the breakdown, at least partially, of the zeolite framework and the creation of extra porosity [60]. It is this disruption of the unit cell long-range order that results in the loss of crystallinity observed. Under the more extreme conditions, NaOH concentrations ≥0.055 M, the solid is converted into an amorphous alumina silicate state and thus no longer a zeolitic material, consistent with studies by García et al [61] and Zhu et al [62]. Figure S1(b) shows aqueous sulfonation of HY zeolites resulted in significantly less of an impact relative to the alkaline treatment, with, where the zeolite framework was still present in the support it was preserved post sulfonic acid deposition. Interestingly, though, a greater degree of crystallinity loss occurs when grafting in water rather than toluene, which coincides with a greater degree of sulfur incorporation. We attribute this to an increase in grafting sites generated by further hydrolysis of the framework (as identified by the drop in crystallinity in table 1).

N₂ adsorption-desorption isotherms of the four commercial zeolites and their corresponding sulfonated versions are shown in figure 2. All exhibit IUPAC type IV isotherms, with H4 hysteresis, indicative of mesoporosity. While the original structure remains after sulfonic acid functionalisation, concurring with XRD findings, the volume of mesoporosity decreases (less apparent hysteresis), with quantitative analysis summarised in table 1. Surface areas, total and external (which incorporates mesopores and macropores), and pore volumes, both microporous and mesoporous, all decline after sulfonation. The impact is greatest for SO₃H/HY-H₂O, which coincides with it possessing the highest sulfur loading (table 1), with a reduction of 84% in total surface area and a 52% decrease in total pore volumes. A direct correlation between the degree of grafting, i.e. sulfur incorporation, and a decrease in porosity is clear, as shown in figure S2 [63]. Thus, the drop in porosity is indicative of either incorporation of acid sites within the pores or grafting across them, i.e. capping them, an issue more likely to impact microporosity. Sulfur content from CHNS elemental analysis, reported in table 1, reveals an increase in grafting efficiency when switching grafting solvent to water, consistent with the work of Pirez et al [24]. Furthermore, as shown in figure S3, S loading displays the direct linear correlation with increased acid site loading, i.e. consistent with S incorporation introducing new acidity. FTIR spectra of pyridine adsorption for HY and SO₃H/HY-H₂O, presented in figure S4, reveal IR bands at \sim 1545 cm⁻¹, 1490 cm⁻¹ and 1450–1445 cm⁻¹ for the parent zeolite, confirming the existence of both Lewis and Brønsted acidity. In contrast, the grafting of sulphonic acid groups, i.e. in $SO_3H/HY-H_2O_3$, results in the loss of Lewis acidity, with no peak observed at 1450–1445 cm⁻¹. Thus, grafting positively influences the Brønsted acidity of the catalysts, which in turn should be beneficial in the promotion of fructose dehydration.

Figure S5 displays N₂ adsorption–desorption isotherms of the hierarchical HY series and their corresponding sulfonated versions. Desilication at low NaOH concentrations, i.e. HY-0.001 and HY-0.01, results in retention of the type IV isotherms with H4 hysteresis of the parent HY zeolite, in agreement with XRD and further evidence that the framework architecture is not negatively impacted. As observed previously, acid site grafting within these two zeolites results in a drop in porosity (table 1). In contrast, HY zeolites treated with higher NaOH concentration show a transition from H4 to H1 hysteresis, with a significant increase in mesopore volume and a simultaneous drop in microporosity. This is evidence of a



 Table 1. Characterisation of catalysts to show various physicochemical properties.

Catalysts	Crystallinity (%)	$\begin{array}{c}S_{BET}\\(m^2 g^{-1})\end{array}$	$\frac{S_{external}}{(m^2 g^{-1})}^a$	V_{micro}^{a} (cm ³ g ⁻¹)	V_{meso}^{b} (cm ³ g ⁻¹)	Sulfur content ^c (%)	Acid capacity ^d $(\mu \text{mol g}^{-1})$
НҮ	100	813 ± 81	225 ± 23	0.27 ± 0.03	0.27 ± 0.03	_	7.3 ± 0.4
SO ₃ H/HY-Tol	91	372 ± 37	90 ± 9	0.13 ± 0.01	0.12 ± 0.01	4.2 ± 0.001	$\textbf{29.8} \pm \textbf{1.3}$
SO ₃ H/HY-H ₂ O	79	127 ± 13	40 ± 4	0.04	0.08 ± 0.01	5.2 ± 0.002	42.4 ± 1.0
HBeta	100	539 ± 54	139 ± 14	0.18 ± 0.02	0.12 ± 0.01	_	9.5 ± 0.3
SO ₃ H/HBeta-Tol	100	380 ± 38	52 ± 5	0.15 ± 0.02	0.08 ± 0.01	2.9 ± 0.001	24.9 ± 0.6
HZSM5	100	374 ± 37	111 ± 11	0.12 ± 0.01	0.14 ± 0.01		23.4 ± 0.7
SO3H/HZSM5-Tol	100	161 ± 16	76 ± 8	0.04	0.10 ± 0.01	0.8	24.3 ± 1.0
HMOR	100	520 ± 52	92 ± 9	0.19 ± 0.02	0.12 ± 0.01	_	37.6 ± 1.0
SO3H/HMOR-Tol	100	422 ± 42	57 ± 6	0.16 ± 0.02	0.12 ± 0.01	0.8	50.7 ± 1.1
HY-0.001	44	755 ± 76	188 ± 19	0.26 ± 0.03	0.36 ± 0.04	_	8.6 ± 2.1
HY-0.01	43	785 ± 79	237 ± 24	0.25 ± 0.03	0.38 ± 0.04		6.7 ± 0.8
HY-0.055	_ ^e	145 ± 15	127 ± 13	0	0.47 ± 0.05		1.8 ± 0.3
HY-0.1	_ ^e	158 ± 16	156 ± 16	0	0.48 ± 0.05	_	1.7 ± 0.3
SO ₃ H/HY-0.001-H ₂ O	31	224 ± 22	86 ± 9	0.06 ± 0.01	0.16 ± 0.02	5.7 ± 0.002	46.6 ± 0.1
SO ₃ H/HY-0.01-H ₂ O	31	221 ± 22	49 ± 5	0.11 ± 0.01	0.19 ± 0.02	5.1 ± 0.002	42.8 ± 0.0
SO ₃ H/HY-0.055-H ₂ O	_ ^e	69 ± 7	69 ± 7	0	0.22 ± 0.02	2.9 ± 0.001	24.2 ± 2.2
SO ₃ H/HY-0.1-H ₂ O	_ ^e	72 ± 7	66 ± 7	0	0.22 ± 0.02	3.1 ± 0.001	24.7 ± 2.4

 \overline{a} by *t*-plot method.

^b $V_{meso} = V_{total (BET)} - V_{micro(t-plot).}$

^c determined by CHNS analysis.

^d determined by ion exchange and pH measurement.

^e destruction of the crystalline phase by the treatment yields an amorphous structure.

6



Figure 2. N₂ adsorption-desorption isotherms: (a) HY, SO₃H/HY-Tol and SO₃H/HY-H₂O, (b) HBeta and SO₃H/HBeta-Tol, (c) HZSM5 and SO₃H/HZSM5-Tol, (d) HMOR and SO₃H/HMOR-Tol.

significant transformation of the porous nature of the materials and is consistent with the complete atomic level restructuring shown by XRD. Furthermore, this restructuring results in a simultaneous drop in total surface area and an increase in average mesopore diameter (figure S6), jumping from 3.8 nm (HY, HY-0.001, and HY-0.01) to 6.5 nm and 7.8 nm for HY-0.1 and HY-0.055, respectively. However, even with such dramatic changes in pore framework structure, grafting of sulfonic acid sites still imparts a drop in porosity.

SEM, shown in figures S7–S9, reveals that neither sulfonation nor NaOH treatment impacts zeolite morphology [21, 64]. For example, it is possible to observe retention of the octahedral morphology of all materials corresponding to the faujasite type zeolite, even where XRD confirm complete destruction of the zeolite crystalline framework, i.e. for NaOH treatment at concentration ≥ 0.055 M. Moreover, the average particle size shows no significant change in size (the largest decrease in size being only 20% for HY-0.055). Thus, where destruction of the micropore framework does occur, it does not lead to a complete restructuring of the alumina-silicate particle. Furthermore, the absence of observing a second solid species, post-sulfonic acid grafting, discredits the possibility of the inherent acidity of the zeolite support catalysing the self-condensation MPTMS.

The nature of the grafted sulfur species was probed by x-ray photoelectron spectroscopy (XPS), allowing for qualitative and quantitative analysis [65, 66]. Figure S10 illustrates two sulfur species present: a high binding energy species at ~168.5 eV, consistent with sulfonic acid ($R-S(=O)_2-OH$) [65, 66], and a second at ~163.5 eV, corresponding to thiol (-SH) functional groups [65]. In all cases, the second species (thiol) was the minor species with a relative amount of less than 10%.

3.2. Catalytic activity

Reaction condition evaluation was performed by evaluating the green credentials of the parent HY zeolite under various ratios of the biphasic reaction media (figure S11). An aqueous-to-organic volume ratio of 1:2 is shown to be favourable, including surpassing the current state-of-the-art (table S1), with the highest PR of 1.96. a reduction in the use of organic solvents, and elimination of the use of DMSO [12, 13, 67, 68].

7



Figure 3. (a) Fructose conversion, (b) HMF yield (as a function of reaction time) over four non-sulfonated zeolites (HY, HBeta, HZSM5 and HMOR) and their sulfonated versions from fructose dehydration. Reaction conditions: 5 wt% fructose, 2 wt% catalyst loading, 3 cm³ water/4.2 cm³ MIBK: 1.8 cm³ 2-BuOH, 160 °C, 800 rpm, microwave irradiation. The lines represent the trend of fructose conversion and HMF yield as a function of reaction time and are added to aid visualisation.

Fructose dehydration over the commercial zeolites and their sulfonated equivalents using optimal biphasic conditions are shown in figure 3, with fructose dehydration promoted over all catalysts relative to a blank reaction. Despite HMOR possessing the highest Brønsted acidity (table 1) of the parent zeolites, its performance is the poorest, whilst HY and HZSM5 achieve the highest conversion, which in part is attributed to their greater mesoporosity. However, acidity (accessibility and/or strength) is also likely critical, given the significant difference in TOF_{HMF production} of 42 (HZSM5) vs 480 (HY) h⁻¹ (table 2). Thus, HY is more effective in utilising its inherent acidity for fructose dehydration. While this may reflect the fact that it possesses the largest micropore size, they are still smaller than the substrate, especially for a hydrated species [69]. Thus, it is more likely that the elevated mesoporosity of HY is the major contributing factor (table 1 and figure S6).

The positive impact of sulfonation on all zeolites is prominent, with increases of up to ~300% for SO₃H/HBeta-Tol. Moreover, TOFs (table 2) further demonstrate the benefit, which, given this account for acid site loadings, the enhancement can only reflect the greater intrinsic activity of the sulfonic acid sites. This, in turn, means that the Brønsted acid sites of the sulfonic acid are more effective than those originating from the zeolite framework. This arises either from differences in acid strength, which, due to the low thermal stability organic functional group cannot be evaluated by TPD, or accessibility, likely given these sites (due to size) are expected to be predominately within the complementary mesopores present within the zeolites and on external surfaces [33]. However, a combination of the two is also a possibility. Of the four different zeolite frameworks, sulfonic acid functionalised HY (SO₃H/HY-Tol) exhibits optimal green credentials with the lowest E-factor (1.24), PMI (119.75), ξ (139.84) and highest ε (0.00886) and thus is identified as the ideal candidate for further catalyst development studies.

Switching grafting solvent from toluene to water not only addresses catalyst synthesis sustainability, at least partially, but also positively impacts catalyst activity. A significant increase in the initial reaction rate (table 2) is achieved, driven in part by greater grafting efficiency. That is, water increases the density of sulfonic acid sites, which are likewise present, to a higher degree, within accessible mesopores and on external surfaces. However, this higher acid site loading consequently leads to reduced HMF yields after 20 min (figure S12), arising from increased side reactions (figure S13), i.e. humin formation from self and cross (with fructose) polymerisation, which Brønsted acid sites also facilitate, alongside minor levels of formic and levulinic acids from hydration, glucose from isomerisation, and furfural.

The catalytic performance of the alkaline-treated HY zeolites and their corresponding sulfonated versions are reported in table 2 and figure 4. Where the intrinsic zeolite framework is retained, namely HY-0.001 and HY-0.01, conversion and yield improve relative to HY, which is accredited to their greater mesopore volumes (note comparable acid loading for all three), leading to enhanced internal mass transfer. This is further apparent from the TOFs, which show up to a 50% increase with regard to HMF production. Conversely, for HY-0.055 and HY-0.1, in which the zeolite framework is destroyed, poorer performance is observed due to the loss of acid sites. However, the greater accessibility of the acidity that is retained, reflected by large mesopore volumes from N_2 sorption isotherms, does result in greater TOFs, indicating that accessibility truly is key, especially when the majority of the acid sites are residing within micropores as is the case for the

Catalyst	Fructose conv rate $(\mu \text{mol min}^{-1})$	$TOF_{fructose conversion}$ $(min^{-1})^{b}$	HMF production rate (μ mol min ⁻¹)	$\operatorname{TOF}_{\operatorname{HMF production}}$ $(\min^{-1})^{\mathrm{b}}$
Blank	4.42 ± 0.13	1	0.7 ± 0.01	/
HY	3.98 ± 0.14	9.1 ± 0.46	3.5 ± 0.10	8.0 ± 0.40
SO ₃ H/HY-Tol	56.36 ± 1.69	31.5 ± 1.58	45.4 ± 1.36	25.4 ± 1.27
		(22.4 ± 1.12)		(17.4 ± 0.87)
SO ₃ H/HY-H ₂ O	116.65 ± 3.50	45.8 ± 2.29	85.7 ± 2.57	33.1 ± 1.65
		(36.7 ± 1.84)		(25.7 ± 1.28)
HBeta	0.41 ± 0.01	0.7 ± 0.04	2.0 ± 0.06	3.6 ± 0.18
SO ₃ H/HBeta-Tol	49.70 ± 1.49	33.2 ± 1.66	19.6 ± 0.59	13.1 ± 0.65
		(33.3 ± 1.67)		(9.5 ± 0.48)
HZSM5	1.99 ± 0.06	1.4 ± 0.07	1.0 ± 0.03	0.7 ± 0.04
SO ₃ H/HZSM5-Tol	8.47 ± 0.25	5.8 ± 0.29	3.1 ± 0.09	2.1 ± 0.11
		(4.4 ± 0.22)		(1.4 ± 0.07)
HMOR	0.32 ± 0.01	0.1 ± 0.01	1.1 ± 0.03	0.5 ± 0.02
SO ₃ H/HMOR-Tol	5.06 ± 0.05	1.7 ± 0.08	7.9 ± 0.24	2.6 ± 0.13
		(1.5 ± 0.08)		(2.1 ± 0.11)
HY-0.001	4.74 ± 0.14	9.2 ± 0.46	5.6 ± 0.17	13.3 ± 0.66
HY-0.01	4.74 ± 0.14	11.8 ± 0.59	5.1 ± 0.15	14.1 ± 0.71
HY-0.055	2.91 ± 0.03	26.9 ± 0.42	1.5 ± 0.05	16.0 ± 0.80
HY-0.1	2.74 ± 0.08	26.9 ± 1.34	1.6 ± 0.05	18.0 ± 0.90
SO ₃ H/HY-0.001-H ₂ O	110.54 ± 3.32	39.5 ± 1.98	85.7 ± 2.57	30.6 ± 1.53
		(30.3 ± 0.65)		(17.4 ± 0.87)
SO ₃ H/HY-0.01-H ₂ O	117.04 ± 3.51	45.5 ± 2.28	88.0 ± 2.64	34.2 ± 1.71
		(33.7 ± 0.65)		(20.1 ± 1.00)
SO ₃ H/HY-0.055-H ₂ O	85.62 ± 2.57	58.9 ± 2.95	65.6 ± 1.97	45.1 ± 2.26
		(32.0 ± 0.65)		(29.1 ± 1.45)
SO ₃ H/HY-0.1-H ₂ O	92.02 ± 2.76	62.2 ± 3.11	68.3 ± 2.05	46.1 ± 2.31
		(35.3 ± 0.65)		(28.1 ± 1.41)

Table 2. Fructose consumption and HMF production TOFs were calculated using rate over initial 5 min and total and sulfonic acid site
loadings, respectively ^a .

^a Each reaction was performed at 160 °C with 0.06 g of catalyst, 3 cm³ water/4.2 cm³ MIBK: 1.8 cm³ 2-BuOH.

^b Value in parenthesis reflects the contribution from sulfonic acid groups only.



Figure 4. (a) Fructose conversion, (b) HMF yield (as a function of reaction time) over alkaline-treated HY zeolites and their corresponding sulfonated versions using water as the grafting solvent from fructose dehydration. Reaction conditions: 5 wt% fructose, 2 wt% catalyst loading, 3 cm³ water/4.2 cm³ MIBK: 1.8 cm³ 2-BuOH, 160 °C, 800 rpm, microwave irradiation. The lines represent the trend of fructose conversion and HMF yield as a function of reaction time and are added to aid visualisation.

parent HY. As previously, grafting sulfonic acids elevates catalytic activity; however, the introduction of extra mesoporosity via NaOH treatment of the parent zeolite did not show any further benefit, e.g. SO₃H/HY-0.001-H₂O and SO₃H//HY-0.01-H₂O perform comparably with SO₃H/HY-H₂O. This is proposed to arise due to desilication occurring throughout the zeolite framework, i.e. some of the extra mesoporosity generated is only accessible via micropores, and thus, these extra mesopores are not as accessible as

Reaction temp (°C)	Reaction time (min)	HMF yield (µmol)	Consumed energy (kJ)	Energy efficiency $(\mu \text{mol kJ}^{-1} \text{ l}^{-1})$	E-factor	$arepsilon \operatorname{Mol}^\circ \operatorname{C}^{-1} \ \mathrm{min}^{-1}$	ξ
140	75	502	547	102	1.37	5.74×10^{-3}	238
150	45	516	360	159	1.30	$9.19 imes 10^{-3}$	142
160	10	533	122	484	1.23	$4.00 imes 10^{-3}$	31
170	5	537	86	691	1.21	$7.59 imes 10^{-3}$	16

Table 3. Energy efficiency and green metrics of HMF production from fructose at optimal reaction times based on HMF yields over SO₃H/HY-H₂O catalysts^a.

^a Reaction conditions: 5 wt.% fructose, 2 wt.% catalysts loading, 3 cm³ water/4.2 cm³ MIBK: 1.8 cm³ 2-BuOH, 800 rpm, microwave irradiation.

mesopores generated from the surface of the zeolite or the external surface of the zeolite. In contrast, $SO_3H//HY-0.055-H_2O$ and $SO_3H//HY-0.1-H_2O$ initially show significantly lower conversion and HMF yields, resulting from the collapsed pore framework and lower surface area, resulting in lower S/Acid loadings. However, the reduced acidity is beneficial to HMF yield at extended reaction times, greater than 20 min, with reduced humin formation compared with $SO_3H/HY-0.001-H_2O$ and $SO_3H//HY-0.01-H_2O$ (figure S13). A comparison of TOFs reveals an identical trend to the parent zeolites, i.e. the destruction of the zeolite framework is not detrimental to the normalised activity. This is further proof that the overall catalyst performance is governed by acidity, be it from sulfonic or alumina silicate species, on the external surface and within accessible mesopores, i.e. the more facile diffusion to these sites is key. Finally, common TOFs from the sulfonic site alone, across the parent and desilicated HY series, is clear evidence of comparable activity of the grafted sulfonic sites, and thus their deposition must be in comparable accessible pores, i.e. within mesopores and not micropores.

Assessment of grafting success, through elemental analysis (CHNS), reveals sulfonic acid grafting is significantly less than 100% efficient, with SO₃H/HY-H₂O exhibiting a sulfur loading of 5.23%, i.e. only ~15% of the MPTMS is actually grafted onto the zeolite with its use in huge excess. To investigate this and the possibility for more efficient usage of MPTMS, a series of catalysts based on the HY zeolite with theoretical loadings varied from 100% to 10% (assuming 100% grafting efficiency) was produced under identical conditions, being denoted as 0.5% S (10%), 1.1% S (40%), 2.6% S (70%), 4.1% S (100%), respectively. The resulting S and acid loading are reported in table S2 and, as shown in figure S14, reveal a strong linear increase in acid loading with S content (as expected). Moreover, an extrapolated intercept of the trendline (7.4 μ mol g⁻¹) is in excellent agreement with the inherent Brønsted acidity of HY parent zeolite (7.3 μ mol g⁻¹), indicating that the Brønsted sites within the zeolite micropores are not sites for grafting, consistent with the findings of Mitchell *et al* [33]. The impact of varying MPTMS on the performance of the resulting catalysts for fructose dehydration is displayed in figure S15. The less than 100% efficiency of the grafting process (table S2) accounts for lower conversions and yields than expected; however, a comparison of TOFs reveals a common TOF across the series, and therefore, the differences in conversion are solely a result of decreased acid site loadings.

Figure S16 shows the impact of reaction temperatures on the catalytic dehydration of fructose. At elevated temperatures, ≥ 160 °C, and in the presence of SO₃H/HY-H₂O-24 h, HMF yields display a volcano plot as a function of time whilst fructose conversion continues to increase. This drop in preference towards HMF, with extended reaction times, is further evidence of the undesirable formation of humins and other by-products [12, 70, 71]. Dropping reaction temperature to 150 °C and below hinders the rate of fructose dehydration but beneficially impacts HMF selectivity, although with optimal HMF yields taking considerably longer (table 3), with the increase in time outweighing any energy savings from running at lower temperatures. An optimal reaction temperature and time of 170 °C and 5 min achieves the greatest energy efficiency and greenest credentials of catalytic processes, giving rise to a process energy efficiency of 691 μ mol kJ⁻¹ l⁻¹, exceeding that of our previous study by a factor of ~6 [12].

Further insight into the conversion of fructose over SO₃H/HY-H₂O is revealed from reaction kinetics, with kinetic profiles from fructose conversion at differing reaction temperatures, for systems with and without SO₃H/HY-H₂O (figures 5 and S17), employed to evaluate kinetic parameters, i.e. rate constants, reaction orders, and activation energies. First-order kinetics for fructose conversion are confirmed, with activation energy (E_a) and pre-exponential factor (A), derived from Arrhenius plots, with SO₃H/HY-H₂O (141 kJ mol⁻¹,1.83 × 10¹⁶ min⁻¹) exhibiting a comparable E_a to values reported for strong homogeneous acid catalysts (namely HCl) [72, 73].

Catalyst reusability was investigated under optimised reaction conditions, with the corresponding results shown in figure 6. Whilst initial retainment of performance was observed (run 2), an increasing drop in



Figure 5. (a) Kinetic profiles of fructose-to-HMF conversion over SO₃H/HY-H₂O catalysts; (b) Arrhenius plot of the formation of HMF from fructose over SO₃H/HY-H₂O catalysts. Reaction conditions: 5 wt.% fructose, 2 wt.% catalysts, 3 cm³ water/4.2 cm³ MIBK: 1.8 cm³ 2-BuOH, 800 rpm, microwave irradiation.



HMF yield occurred over runs 3–5, with TOF dropping to less than 20% of the fresh catalyst (table S4). This decline is attributed to two factors: (i) deposition of humins on the catalyst, which water nor acetone can remove, leading to pore and active site blockage, as confirmed by an increase in carbon content, and (ii) decreased S loading, due to C deposition, S leaching, or a combination (table S4). Gupta *et al* [21] and Bisen *et al* [19] have reported the use of H_2O_2 to regenerate the activity of sulfonic acid catalytic sites. Replicating this reactivation approach, under identical conditions to the original synthesis, restored SO₃H/HY-H₂O to its initial white colour and reinstated ~90% of initial performance. Moreover, the successful regeneration of the catalyst via H_2O_2 treatment confirms that the deactivation initially observed arises from C deposition and not leaching of the sulfonic acid functionality.

The potential of the optimal SO₃H/HY-H₂O catalyst was explored for its performance towards the conversion of glucose, being benchmarked against a blank reaction under the optimal condition identified from the fructose studies (figure S18). This represents a further step in lignocellulose valorisation, with glucose seen as the precursor to fructose, via isomerisation, in the overall process. There is clearly a significant impact resulting from the presence of SO₃H/HY-H₂O, with conversion increasing by a factor of 2.5, whereas HMF yield shows an increase of a factor of 10. Thus, while SO₃H/HY-H₂O is only mildly effective in promoting glucose conversion, due to the absence of Lewis acidity (figure S4), it significantly impacts HMF production. Thus, the aim would appear to be the engineering of catalytic systems with a balance of Lewis acidity (for glucose isomerisation) and Brønsted acidity (for fructose dehydration) if expanding HMF production beyond fructose to glucose and glucose-containing carbohydrates is to be realised.

Benchmarking the overall sustainability of the catalytic process against current state-of-the-art solid acid catalysts reported is depicted in figure 7, with full details in table S5. The coupling of SO₃H/HY-H₂O within



a biphasic reaction media under microwave irradiation performs highly favourably, increasing the sustainability of the process [52, 53, 55], relative to other zeolites [11, 12, 43], and while SAPO-44 [74] does show superior HMF yields, longer reaction times harm its claim for being a more sustainable system owing to increased energy use. Likewise, $SO_3H/HY-H_2O$ is preferable to other sulfonic acid-based catalysts, e.g. via deposition on MCM-41 [75] and SBA-15 [76].

4. Conclusions

The development of a sustainable chemical industry demands innovative use of current catalytic materials, in particular for biomass conversion to chemicals of interest, such as HMF. Zeolites and hierarchical zeolites, the latter resulting from the enhanced introduction of complementary mesoporosity, represent ideal candidates for functionalisation with sulfonic acid sites, which in turn are prime of subsequent deployment in fructose dehydration. Increased highly accessible mesoporosity facilitates sulfonic acid incorporation, which elevates fructose conversion and maximises HMF yields, with the additional acidity from sulfonic acid sites dramatically enhancing catalytic performance relative to the inherent acidity of the zeolite framework. However, yields from the sulfonic acid functionalised materials are highly sensitive to reaction duration, with extended durations imparting a negative influence on yields from the further reaction of HMF into carboxylic acids and humins. Catalyst performance within a biphasic reaction medium (water/MIBK: 2-BuOH (7:3)) under microwave irradiation, with the optimal catalyst (SO₃H/HY-H₂O), leads to 64% HMF yields within only 5 min at 170 °C, which results in optimal green credentials, specifically energy economy coefficient (7.59×10^{-2}) , due to the significantly reduced reaction duration. Moreover, the destruction of the zeolite framework via harsher desilication conditions is shown not to be excessively detrimental to the resulting performance of supported sulfonic acid sites, with TOFs comparable irrespective of the support they are grafted to. This indicates that accessibility is key, given that these can be predicted not to reside within micropores due to their size. A final benefit of sulfonic acid incorporation as a route to catalyst production for fructose dehydration to HMF is facile catalyst reactivation through stirring in an aqueous H_2O_2 solution.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary information files).

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