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# Bifunctional Solid Catalysts for the Selective Conversion of Fructose to 5-Hydroxymethylfurfural

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**Abstract** Solid catalysts based on SBA-15 silica were designed for the conversion of fructose to 5-hydroxymethylfurfural (HMF). The catalysts incorporate thioether groups that may promote the tautomerization of fructose to its furanose form, as well as sulfonic acid groups to catalyze its dehydration. The materials were characterized by elemental analysis, X-ray diffraction, N<sub>2</sub> adsorption/desorption, and solid-state <sup>13</sup>C and <sup>29</sup>Si CP/MAS NMR spectroscopy. Functional groups incorporated into mesoporous silica by co-condensation are more robust under the reaction conditions (water at 180 °C) than those grafted onto a non-porous silica. The bifunctional mesoporous catalyst achieved a selectivity for HMF of 74% at 66% fructose conversion.

**Keywords** Hydroxymethylfurfural · Fructose · SBA-15 · Solid-state NMR · Dehydration · Bifunctional catalyst

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## 1 Introduction

Future supplies of energy, chemicals and materials depend on developing renewable alternatives to petroleum, for which biomass represents a sustainable source of carbon-based precursors. The US generates 1.3 billion tons of non-food biomass yearly, containing the energetic equivalent of 3 billion oil barrels [1], however, little of this material is currently used for chemical production [2]. Carbohydrates are a key biomass component and an important potential source of chemical intermediates, but they are poorly compatible with conventional chemical conversion technologies. In particular, the large-scale, selective transformation of carbohydrates to platform chemicals will require the development of new, functional-group-tolerant catalysts compatible with continuous processing.

A potential replacement for some petroleum-based feedstocks that is made readily from carbohydrates is 5-hydroxymethylfurfural (HMF) [3]. It can serve as a precursor to numerous products and chemical intermediates relevant to the fuel, polymer, and pharmaceutical industries [4–9]. Selective hydrogenation gives a fuel additive with combustion properties similar to ethanol, and superior diesel miscibility [10]. Biodiesel and jet fuel may be synthesized by hydrogenating the aldol-condensation products of HMF [5, 6]. A polyethylene terephthalate (PET) analog can be prepared from HMF derivatives [5]. Selective oxidation of HMF leads to 2,5-furandicarboxylic acid (FDCA), a potential replacement for terephthalic acid [11]. Reduction of HMF to 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)tetrahydrofuran produces the alcohol linkers of this PET analog.

HMF can be obtained by the acid-catalyzed dehydration of fructose, glucose, sucrose and even cellulose [7, 8, 12–14]. Recently, a tandem process combining an isomerase

enzyme and an acid dehydration catalyst was employed to produce HMF from glucose [15]. For these systems, the dehydration reaction is complicated by competing pathways, including reversion, fragmentation and polymerization [9]. Mineral acid catalysts such as HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> have been employed, at temperatures ranging from 80 to 350 °C [8]. Using HCl in water, a typical selectivity for HMF from fructose is 50% at 50% conversion [8, 9]. There are proposed mechanisms involving either acyclic or cyclic intermediates [11], however, isotope-labeling studies suggest that HMF is produced via three consecutive losses of water from the cyclic furanose tautomer, Scheme 1 [16]. Temperature and the presence of co-solvents play an important role in the selectivity of acid-catalyzed fructose dehydration, due to their effects on the furanose-pyranose tautomer equilibrium [17]. Increasing the reaction temperature increases selectivity to HMF, which is less likely to undergo rehydration or polymerization at higher temperature [8]. At 180 °C, using HCl as the catalyst in a solvent mixture comprised of water, methyl isobutyl ketone and 2-butanol, an HMF selectivity of 80% was achieved at 86% fructose conversion [9]. Similar selectivities have been reported for solid acid catalysts such as PK-216, Amberlyst 15, H-Mordenite, and Nafion NR50 [9, 18]. Higher selectivity can be achieved by addition of dimethylsulfoxide (DMSO) or dimethylformamide (DMF) as promoters [17, 19, 20], however, product isolation is complicated by their high boiling points [21].

In principle, the need for corrosive mineral acid catalysts and high boiling components could be eliminated by the use of a supported catalyst that contains both acid and promoter functions. Silica, which is only weakly acidic, is

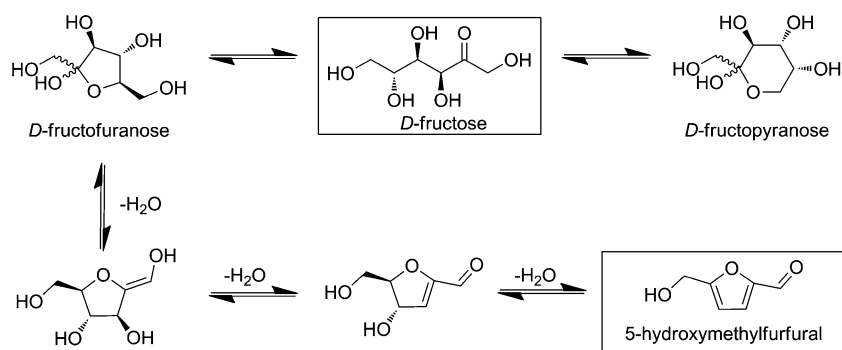
well-suited as a solid support for bifunctional catalysts. Its surface is readily modified either by post-synthetic grafting [22] or by co-condensation during its synthesis [23, 24]. In particular, an anchored thiol can serve as a precursor to both the desired promoter and acid sites, Scheme 2. The resulting thioalkylsilicon groups (Si(CH<sub>2</sub>)<sub>n</sub>SH) may be attached to the silica framework via one, two, or three siloxane bonds. These T<sup>1</sup>, T<sup>2</sup> and T<sup>3</sup> sites are readily distinguished by <sup>29</sup>Si solid-state NMR [25]. The relative abundance of each T site depends on the silica modification technique. In post-synthetic modification, the density of functional groups is limited by the number of accessible silanols, and grafting results in a large fraction of T<sup>1</sup> relative to T<sup>2</sup> sites. In contrast, the co-condensation route is not dependent upon the surface silanol concentration, so higher functional group loadings can be achieved. It produces mostly T<sup>2</sup> and T<sup>3</sup> sites, which tend to be more stable hydrothermally than T<sup>1</sup> sites. In particular, SBA-15 is a robust material with a highly-ordered 2D hexagonal pore structure; furthermore, it is readily functionalized by co-condensation of TEOS with, for example, a thiopropylsilane [26].

## 2 Experimental Section

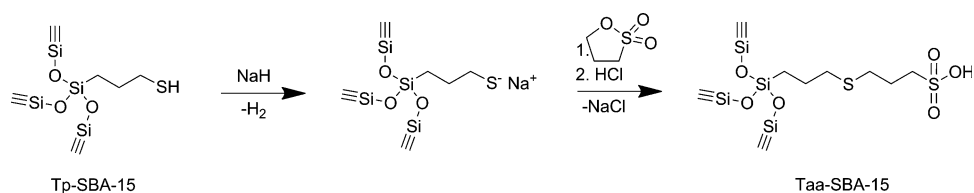
### 2.1 Reagents and Materials

Tetraethyl orthosilicate (TEOS, >98%), (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%), 1-butanethiol (99%), sodium hydride (60% dispersion in mineral oil), 1,3-propanesultone (≥99%), ethyl acetate (ACS reagent grade),

**Scheme 1** Tautomer equilibria of D-fructose: the β-D-pyranose form is favored in water at room temperature, but the equilibrium shifts toward the β-D-furanose form in DMSO [11, 14]



**Scheme 2** Proposed synthetic scheme for a bifunctional acid catalyst supported on silica



fructose and 2-butanol were purchased from Aldrich and used as received. Pluronic P123 was obtained from BASF. Hexanes (ACS reagent grade) and methyl isobutyl ketone (MIBK) were purchased from Fisher Scientific. Ethanol (200 proof, Gold Shield) was used as received. THF and diethyl ether (Aldrich) were purified by passage through two neutral  $\text{Al}_2\text{O}_3$  columns. Toluene (Aldrich) was purified by passage through one column containing alumina and a second packed with  $\text{CuO}/\text{Al}_2\text{O}_3$  (Q5). A solution of ethereal HCl (0.500 M) was prepared by reaction of acetyl chloride (3.56 mL, 0.0500 mol; Aldrich, 98%) with methanol (2.03 mL, 0.0500 mol; Aldrich, spectrophotometric grade) in 500 mL dry diethyl ether. Amberlyst-70 was obtained from Rohm & Haas. A non-porous, fumed Aerosil silica (A380), with a surface area of ca. 380  $\text{m}^2/\text{g}$  and a primary particle size of 7 nm, was supplied by Degussa. Unmodified SBA-15 was prepared following a literature procedure [23, 27]. All dry materials were stored in an argon-filled glove box to prevent re-adsorption of atmospheric moisture.

## 2.2 Characterization

Solution-state NMR spectra were recorded on a Bruker SPX200 SB spectrometer operating at 4.7 T. Solid-state NMR spectra were recorded on a Bruker DSX300 WB spectrometer operating at 7.00 T, with frequencies of 75.4 and 59.7 MHz for  $^{13}\text{C}$  and  $^{29}\text{Si}$ , respectively. Samples were packed under an argon atmosphere into 4 mm zirconia rotors (Bruker).  $^{29}\text{Si}$  cross-polarization/magic angle spinning (CP/MAS) spectra were obtained using a  $90^\circ$  pulse length of 3.00  $\mu\text{s}$ , a contact time of 5 ms, and high power proton decoupling during detection. Typically, 25,000 scans were acquired at a spinning rate of 6 kHz. Chemical shifts were referenced to tetrakis(trimethylsilyl)silane.  $^{13}\text{C}$  CP/MAS spectra were obtained using a  $90^\circ$  pulse length of 3.7  $\mu\text{s}$ , a contact time of 2 ms, and high power proton decoupling during detection. Typically, 25,000 scans were acquired at a spinning rate of 10 kHz. Chemical shifts were referenced to adamantane.

Powder X-ray diffraction (XRD) was collected from 0.6 to  $4^\circ$  [ $2\theta$ ], using a SCINTAG PADX diffractometer with  $\text{Cu K}_\alpha$  radiation (0.02° resolution).  $\text{N}_2$  adsorption/desorption measurements were obtained on a Micromeritics TriStar 3000 Porosimeter. Elemental analysis was performed by Desert Analytics (Tuscon, AZ).

## 2.3 Synthesis of 3-(Butylthio)propane-1-Sulfonic Acid (BTPSA)

To a 100 mL round-bottomed flask containing dry THF (25 mL), 1-butanethiol (500  $\mu\text{L}$ , 4.67 mmol) was added under flowing  $\text{N}_2$ . After cooling to  $-78^\circ\text{C}$ , sodium hydride

(0.280 g, 7.01 mmol) was added over 15 min and the mixture was stirred for 30 min. 1,3-Propanesultone (820  $\mu\text{L}$ , 9.34 mmol) was added and the mixture was stirred for 12 h, while warming slowly to room temperature. The reaction was quenched with deionized water (50 mL). After stirring for 15 min, the solution was transferred to a separatory funnel and extracted with hexanes ( $3 \times 50$  mL), followed by ethyl acetate ( $3 \times 50$  mL). The aqueous layer was acidified with 20 mL ethereal HCl (0.50 M) and washed with diethyl ether ( $2 \times 20$  mL). BTPSA was recovered as a viscous oil from the combined organic layers on a rotary evaporator (0.1 mTorr).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.1 (s, 1H), 3.20 (t, 2H), 2.63 (m, 2H), 2.47 (m, 2H), 2.05 (m, 2H), 1.54 (m, 2H), 1.42 (m, 2H), 0.91 (t, 3H).  $^{13}\text{C}$  NMR (50.32 MHz,  $\text{CDCl}_3$ ):  $\delta$  50.00 ( $\text{CH}_2\text{SO}_3\text{H}$ ), 30.83 ( $\text{CH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$ ), 30.66 ( $(\text{C}_3\text{H}_7)\text{CH}_2\text{S}$ ), 29.66 ( $(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{S}$ ), 24.16 ( $\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ ), 21.16 ( $\text{CH}_3\text{CH}_2$ ), 12.83 ( $\text{CH}_3$ ).

## 2.4 Grafting of Thiopropyl Groups onto Non-Porous Silica (Tp-A380)

Aerosil A380 (1.00 g) was dried by heating to  $100^\circ\text{C}$  under vacuum (0.1 mTorr) for 12 h, then suspended in 50 mL toluene. MPTMS (400  $\mu\text{L}$ , 2.05 mmol) was added and the mixture was refluxed for 15 h. The solid was washed with ethanol ( $3 \times 15$  mL), isolated by centrifugation, and dried at  $100^\circ\text{C}$  under vacuum (0.1 mTorr) for 12 h.  $^{13}\text{C}$  CP/MAS NMR:  $\delta$  9 ( $\text{SiCH}_2$ ), 27 ( $\text{CH}_2\text{CH}_2\text{SH}$ ), 50 ( $\text{SiOCH}_3$ ).  $^{29}\text{Si}$  CP/MAS NMR:  $\delta$   $-48$  ( $\text{T}^1$ ),  $-57$  ( $\text{T}^2$ ),  $-100$  ( $\text{Q}^3$ ),  $-110$  ( $\text{Q}^4$ ). Sulfur analysis: 1.16 wt%.

## 2.5 Installation of Propylsulfonic Acid Groups on Tp-A380 (Taa-A380)

Tp-A380 (1.00 g) was transferred to a 100 mL two-necked round-bottomed flask under  $\text{N}_2$ . Dry THF (25 mL) was added and the flask was cooled to  $-78^\circ\text{C}$ . A suspension of NaH (400 mg, 10.0 mmol) in 10–15 mL THF was transferred via cannula over 15 min. After 30 min, 1,3-propanesultone (1.30 mL, 15.0 mmol) was added dropwise. The mixture was stirred for ca. 12 h, while the flask warmed slowly to room temperature. The reaction was quenched with deionized water (50 mL). The solid was collected by filtration and washed with hexanes ( $3 \times 50$  mL), ethyl acetate ( $3 \times 50$  mL), ethereal HCl (50 mL, 0.50 M), then fresh methanol ( $3 \times 50$  mL). The modified silica was dried at  $100^\circ\text{C}$  under vacuum (0.1 mTorr) for 12 h.  $^{13}\text{C}$  CP/MAS NMR:  $\delta$  50 ( $\text{CH}_2\text{SO}_3\text{H}$ ;  $\text{SiOCH}_3$ ), 30 ( $\text{CH}_2\text{SCH}_2$ ), 27 ( $\text{CH}_2\text{CH}_2\text{SH}$ ), 24 ( $\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ ,  $\text{SiCH}_2\text{CH}_2$ ), 11 ( $\text{SiCH}_2$ ).  $^{29}\text{Si}$  CP/MAS NMR:  $\delta$   $-48$  ( $\text{T}^1$ ),  $-57$  ( $\text{T}^2$ ),  $-100$  ( $\text{Q}^3$ ),  $-110$  ( $\text{Q}^4$ ). Sulfur analysis: 1.20 wt%.

## 2.6 Synthesis of Thiopropyl-Functionalized Mesoporous Silica (Tp-SBA-15)

Following a modified literature procedure [28], Pluronic P123 (2.00 g) was dissolved with stirring in 1.90 M aqueous HCl (57.5 mL) and heated to 40 °C in a 300 mL pressure reactor (Parr) equipped with a Teflon liner. TEOS (4.1 mL, 18.5 mmol) was added, followed 45 min later by MPTMS (381  $\mu$ L, 1.95 mmol). After 24 h, the temperature was increased to 100 °C for a further 24 h. The resulting suspension was filtered and washed with ethanol. The surfactant was removed by Soxhlet extraction with ethanol for 24 h. The resulting solid was dried at room temperature in air overnight, then at 100 °C under vacuum (0.1 mTorr) for 12 h.  $^{13}\text{C}$  CP/MAS NMR:  $\delta$  11 ( $\text{SiCH}_2$ ), 17 (P123), 28 ( $\text{CH}_2\text{CH}_2\text{SH}$ ), 59 (P123), 75 (P123).  $^{29}\text{Si}$  CP/MAS NMR:  $\delta$  -57 ( $\text{T}^2$ ), -66 ( $\text{T}^3$ ), -100 ( $\text{Q}^3$ ), -110 ( $\text{Q}^4$ ). Sulfur analysis: 3.46 wt%.

## 2.7 Installation of Propylsulfonic Acid Groups on Tp-SBA-15 (Taa-SBA-15)

The reaction conditions used for modifying Tp-A380 were also used for Tp-SBA-15.  $^{13}\text{C}$  CP/MAS NMR:  $\delta$  11 ( $\text{SiCH}_2$ ), 24 ( $\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ ;  $\text{SiCH}_2\text{CH}_2$ ), 30 ( $\text{Si}(\text{CH}_2)_2\text{CH}_2\text{SCH}_2$ ), 34 ( $\text{SiCH}_2)_3\text{SCH}_2$ ), 50 ( $\text{CH}_2\text{SO}_3\text{H}$ ;  $\text{SiOCH}_3$ ), 70 (P123).  $^{29}\text{Si}$  CP/MAS NMR:  $\delta$  -57 ( $\text{T}^2$ ), -66 ( $\text{T}^3$ ), -100 ( $\text{Q}^3$ ), -110 ( $\text{Q}^4$ ). Sulfur analysis: 7.59 wt%.

## 2.8 Catalytic Dehydration of Fructose

All reactions were carried out using 50 mg solid catalyst, 1.5 g fructose in deionized water (30 wt%), and 3.0 g MIBK: 2-butanol (7:3 w/w). The benchmark catalyst Amberlyst 70 was washed with Milli-Q water, dried at 120 °C overnight, and crushed. The modified silicas were washed with Milli-Q water and dried overnight under partial vacuum (163 Torr) at 110 °C. Reactions were carried out in thick-walled glass reactors (10 mL, Alltech) in a 16-well oil-filled aluminum block maintained at 180 °C. The reactors were sealed using Teflon liners (Alltech) inserted into plastic caps that were cooled during the reaction by a stream of flowing air and stirred using triangular magnetic stirring bars. Reactions were quenched by submerging the reactors in an ethylene glycol bath cooled with dry ice.

The aqueous and organic layers were analyzed using a Waters e2695 HPLC system equipped with a 2998 photodiode array detector and a 2414 refractive index detector. In a typical reaction, the fructose and HMF contents of each phase were analyzed with an Aminex HPX-87P column (Biorad) at 85 °C, using Milli-Q water as the mobile phase at a flow rate of 0.6 mL  $\text{min}^{-1}$ . The disappearance of

fructose was monitored using a refractive index detector, while HMF production was monitored using a UV detector (320 nm). Fructose conversion and HMF selectivity were calculated using the volumes of the aqueous and organic layers after reaction.

## 3 Results and Discussion

### 3.1 Synthetic Strategy for the Modification of Silica

The feasibility of the reactions shown in Scheme 2 were first explored in solution. The reaction of 1-butanethiolate (Tb) with 1,3-propanesultone gave 3-(butylthio)propane-1-sulfonate (BTPSA) [29]. The identity of the product was confirmed by NMR. Two signals for the methylene carbons bonded directly to the thioether S were observed, at 30.83 and 30.63 ppm. The signature  $^{13}\text{C}$  resonance of the sultone ring (69.9 ppm, CO) was not detected, implying that it had reacted completely. The characteristic  $C_\beta$  signal of 1-butanethiol, at ca. 35 ppm, was also absent.

### 3.2 Modification of Non-Porous Silica by Post-Synthetic Grafting

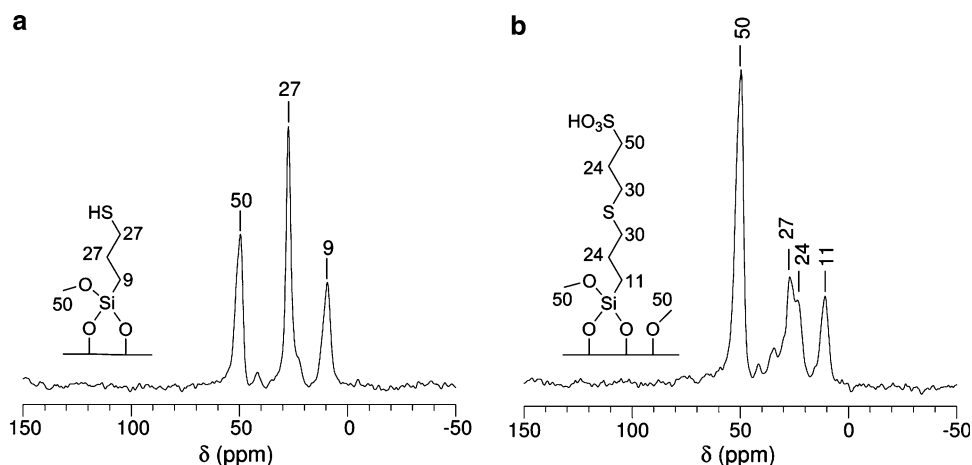
Thiopropyl-modified A380 (Tp-A380) was synthesized by the reaction of MPTMS with the surface hydroxyls of non-porous silica. The expected resonances of the thiopropyl groups [23] were observed in the  $^{13}\text{C}$  CP/MAS NMR spectrum, Fig. 1a. The  $^{29}\text{Si}$  CP/MAS spectrum reveals monoalkylsilicon signals at -48 ( $\text{T}^1$ ) and -57 ppm ( $\text{T}^2$ ), Fig. 2a. The surface area and thiopropyl loading (inferred from sulfur analysis) are shown in Table 1.

We attempted to use the sultone ring-opening reaction (described above) to modify the surface of Tp-A380 with propylsulfonic acid groups. The  $^{13}\text{C}$  CP/MAS spectrum in Fig. 1b confirms that the reaction occurred to a limited extent, as judged by the appearance of the signal at 24 ppm. However, the signal at 27 ppm suggests the persistence of unmodified thiopropyl groups. While  $^{29}\text{Si}$  CP/MAS NMR signal intensities are not quantitative, it is clear that the  $\text{T}^1$ : $\text{T}^2$  ratio is much lower than in Tp-A380, Fig. 2b. The increase in sulfur loading is negligible, from 1.16 to 1.20 wt% (i.e., from 0.36 to 0.38 mmol/g). These observations are consistent with extensive cleavage of  $\text{T}^1$  sites under the synthesis and/or workup conditions. The decrease in the  $\text{Q}^3$ / $\text{Q}^4$  ratio also suggests structural reordering and increased condensation of the silica framework.

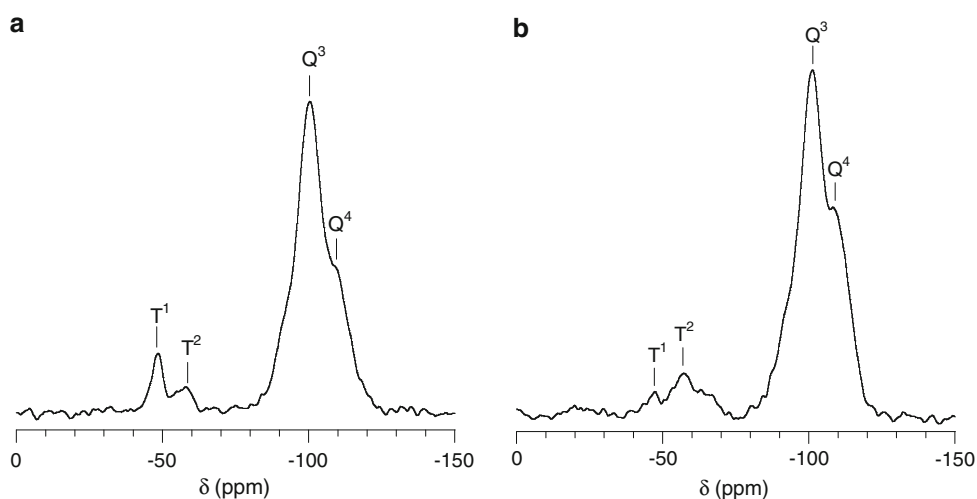
### 3.3 Functionalization of Silica by Co-condensation

To increase the loading of the anchored bifunctional promoter/catalyst and its hydrothermal stability, thiopropyl

**Fig. 1** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra for **a** Tp-A380; and **b** Taa-A380



**Fig. 2** Solid-state  $^{29}\text{Si}$  CP/MAS NMR spectra for **a** Tp-A380; and **b** Taa-A380



**Table 1** Physicochemical properties of supported catalysts

Material	Sulfur loading (mmol/g)	Surface area ( $\text{m}^2/\text{g}$ )	Pore size <sup>a</sup> (nm)	Mesopore structure <sup>b</sup>
Amberlyst 70	–	36 <sup>c</sup>	22 <sup>c</sup>	–
Tp-A380	0.36	360	–	–
Taa-A380	0.38	n.a.	–	–
SBA-15	–	850 <sup>d</sup>	8.9 <sup>d</sup>	Ordered
Tp-SBA-15	1.1	444	4.1	Ordered
Taa-SBA-15	2.3	218	7.5	Not ordered

<sup>a</sup> Calculated using the BJH method

<sup>b</sup> Judged by the presence of a basal reflection  $d(100)$  in the powder XRD pattern

<sup>c</sup> Data provided by Rohm and Haas [33]

<sup>d</sup> Literature values for SBA-15 [27]

groups were incorporated into an SBA-15 framework by co-condensation of MPTMS with TEOS [30]. The thiopropyl loading of the resulting Tp-SBA-15, 1.0 mmol/g, is significantly higher than that of Tp-A380 (0.36 mmol/g). The X-ray diffraction pattern of Tp-SBA-15 (see Supplementary material) matches the literature [23, 31]. In particular, a strong  $d(100)$  reflection typical of mesoscopic

hexagonal ordering was observed at  $2\theta = 1.00^\circ$ .  $\text{N}_2$  adsorption/desorption gave a type IV isotherm characteristic of a mesoporous material (see Supplementary material).

The  $^{13}\text{C}$  CP/MAS NMR spectrum in Fig. 3a confirms the presence of anchored thiopropyl groups as well as residual Pluronic P123, the latter incompletely removed by ethanol extraction. The  $^{29}\text{Si}$  CP/MAS spectrum of the

modified silica shows signals for thioalkylsilicon sites at  $-57$  ( $T^2$ ) and  $-66$  ppm ( $T^3$ ), Fig. 4a, in agreement with published assignments [23]. The reaction of Tp-SBA-15 with NaH, followed by 1,3-propanesultone, was used to install propylsulfonic acid groups on the thiol sites. The characteristic signal at 24 ppm confirms that the reaction was successful, Fig. 3b. Unlike for Taa-A380, unmodified thiopropyl groups do not appear to be present. In the  $^{29}\text{Si}$  CP/MAS NMR spectrum, the  $T^2:T^3$  ratio changes little upon conversion of Tp-SBA-15 to Taa-SBA-15, Fig. 4b. Furthermore, the sulfur content of Taa-SBA-15 (2.3 mmol/g) is double that of Tp-SBA-15 (1.1 mmol/g), therefore modification of the anchored thiolpropyl groups appears to be near-quantitative.

Although the XRD pattern of Taa-SBA-15 was expected to be similar to that of Tp-SBA-15, no diffraction peaks were detected (see Supplementary material). The modified silica therefore does not retain mesoscopic ordering upon further derivatization. There are also changes in surface area and average pore diameter (Table 1). We believe competing reactions complicate catalyst synthesis. In

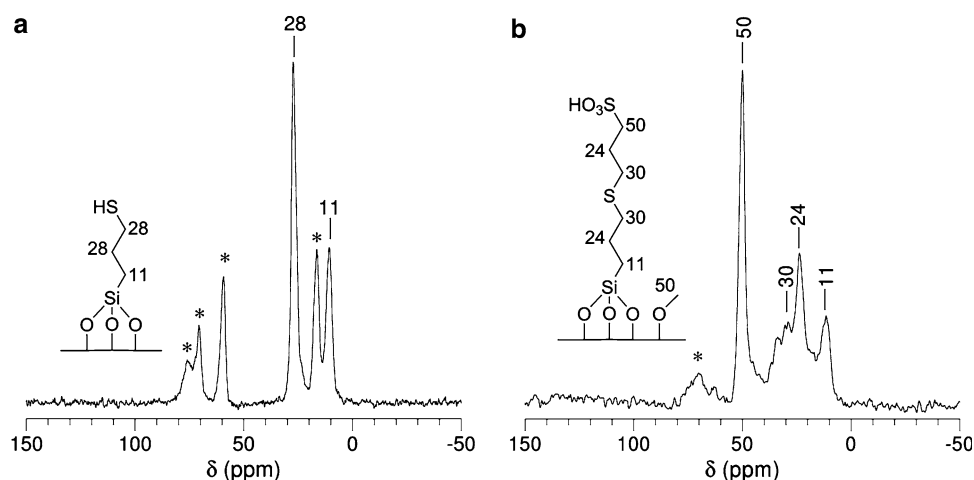
particular, modification of the silica framework order is likely to occur during the deprotonation of anchored thiols with NaH [32]. Framework modification presumably also occurs for Tp-A380 under the same conditions.

### 3.4 Reactivity in Fructose Dehydration

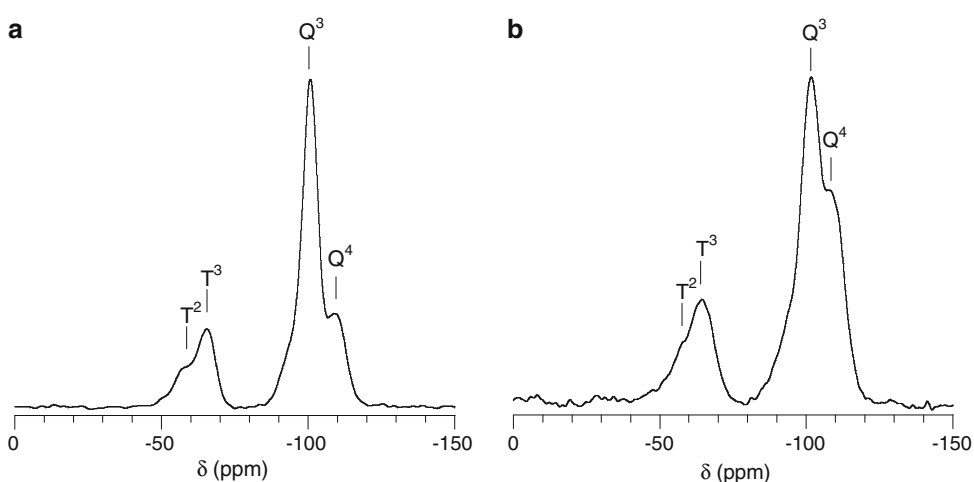
Batch reactions were conducted with both propylsulfonic acid-functionalized silicas (Taa-A380 and Taa-SBA-15). For comparison, unmodified SBA-15 and both thiopropyl-modified silicas (Tp-A380 and Tp-SBA-15) were also tested. The reaction times for Taa-A380, Taa-SBA-15 and the commercial catalyst were adjusted so that high conversion was achieved ( $\geq 60\%$ ), judged visually by the appearance of colored (brown) byproducts. The reaction time was fixed at 120 min for the unfunctionalized and thiopropyl-functionalized silicas.

A commercial solid acid served as the benchmark. Although the phenylsulfonic acid-functionalized polystyrene resin Amberlyst 15 was previously used to produce HMF [13], it is stable only up to 120 °C. Since selectivity

**Fig. 3** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra for **a** Tp-SBA-15; and **b** Taa-SBA-15. Signals from the surfactant are denoted by asterisks



**Fig. 4** Solid-state  $^{29}\text{Si}$  CP/MAS NMR spectra for **a** Tp-SBA-15; and **b** Taa-SBA-15





**Table 2** Comparison of catalytic fructose dehydration by various solid acid catalysts<sup>a</sup>

Catalyst	Reaction time (min)	Fructose conversion (%)	HMF selectivity (%)
Amberlyst 70	10	86 <sup>b</sup>	67 <sup>b</sup>
Tp-A380	120	67	64
Taa-A380	120	62	61
SBA-15	120	59	52
Tp-SBA-15	120	61	52
Taa-SBA-15	30	66	74

<sup>a</sup> The batch reactor contained 50 mg catalyst, 1.5 g aqueous fructose (30 wt%) and 3.0 g MIBK/2-butanol (7:3 w/w). Reactions were conducted at 180 °C under autonomous pressure

<sup>b</sup> Average of five independent experiments. The standard deviations for conversion and selectivity are 9.2 and 0.79%, respectively

for HMF increases with temperature, we chose to conduct our dehydration reactions at 180 °C. Therefore Amberlyst 70, with a maximum operating temperature of 190 °C and an acid content of 2.5 mmol/g, was employed [33]. It reached 86% conversion of fructose after 10 min, but with only 67% selectivity to HMF, Table 2. For Tp-A380 and Taa-A380, a much longer time (120 min) was required to reach high conversion ( $\geq 60\%$ ). Furthermore, the activities of Tp-A380 and Taa-A380 are nearly the same, despite the absence of propylsulfonic acid groups of Tp-A380. This is likely due to the low acid loading of Taa-A380.

Unmodified SBA-15 was tested for its fructose dehydration activity: after 120 min, HMF was produced in 52% selectivity at 59% conversion. The low activity is attributed to the weak Brønsted acidity of the surface silanols [34]. For Tp-SBA-15, the conversion after 120 min had increased to 61%, while the selectivity for HMF remained at 52%. However, the selectivity for HMF over Taa-SBA-15 was higher than for any other catalyst tested here, 74% at 66% conversion. Its selectivity is tentatively attributed to the presence of the thioether, which may act as a reaction promoter. The fructose conversion was also higher for Taa-SBA-15 than for either SBA-15 or Tp-SBA-15 (which were allowed to react four times longer), due to the presence of propylsulfonic acid groups. Although the mesopore ordering of the framework was compromised, our results show that a bifunctional catalyst anchored to silica can be used to convert fructose selectively to HMF.

#### 4 Conclusions

To eliminate the need for mineral acids and soluble reaction promoters in HMF production, bifunctional silicas containing a propylsulfonic acid catalyst and a thioether group as promoter were prepared. The mesoporous silica

prepared by co-condensation incorporated more functional groups than a non-porous silica modified by grafting. The lower acidity and the presence of the thioether as promoter may contribute to the improved selectivity relative to the benchmark catalyst, a supported phenylsulfonic acid. However, activity is limited by the low extent of silica functionalization and, in the case of the porous silica, possibly by the loss of mesoscopic order.

We are investigating alternative synthetic routes to bifunctional silicas with higher functional group loadings that retain the ordered mesopore structure of the silica framework. These pores may alter how water solvates fructose and change the tautomer distribution, similar to the effect of DMSO in homogeneous catalysis. In addition, we will evaluate the promoter effect of the thioether before and after its selective oxidation to the corresponding sulfide or sulfone.

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#### References

- Carole T, Pellegrino J, Paster M (2004) *Appl Biochem Biotechnol* 115:871
- Davenport R (2009) *Ind Biotechnol* 4:59
- Bicker M, Hirth J, Vogel H (2003) *Green Chem* 5:280
- Gupta P, Singh SK, Pathak A, Kundu B (2002) *Tetrahedron* 58:10469
- Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) *Science* 308:1446
- Kunkes EL, Simonetti DA, West RM, Serrano-Ruiz JC, Gartner CA, Dumesic JA (2008) *Science* 322:417
- Moye CJ (1964) *Rev Pure Appl Chem* 14:161
- Kuster BFM (1990) *Starch* 42:314
- Roman-Leshkov Y, Chheda JN, Dumesic JA (2006) *Science* 312:1933
- Ras E, Maisuls S, Haesackers P, Gruter G, Rothenberg G (2009) *Adv Synth Catal* 351:3175
- Lewkowsky J (2001) *Arkivoc* 2:17
- Zhao H, Holladay JE, Brown H, Zhang ZC (2007) *Science* 316:1597
- Yong G, Zhang Y, Ying JY (2008) *Angew Chem Int Ed Engl* 47:9345
- Su Y, Brown HM, Huang X, Zhou X-D, Amonette JE, Zhang ZC (2009) *Appl Catal A Gen* 361:117
- Renliang H, Qi W, Su R, He Z (2010) *Chem Commun* 46:1115
- Perez Locas C, Yaylayan VA (2008) *J Agric Food Chem* 56:6717
- Dais P, Perlin AS (1985) *Carbohydr Res* 136:215



18. Gandini A, Belgacem MN (1997) *Prog Polym Sci* 22:1203
19. Shimizu K, Uozumi R, Satsuma A (2009) *Catal Commun* 10:1849
20. Dais P, Perlin AS (1987) *Carbohydr Res* 169:159
21. Antal MJ, Mok WS, Richards GN (1990) *Carbohydr Res* 199:91
22. Vansant EF, Van Der Voort P, Vrancken KC (1995) *Stud Surf Sci Catal* 93:149
23. Margolese D, Melero JA, Christiansen SC, Chmelka BF, Stucky GD (2000) *Chem Mater* 12:2448
24. Burkett SL, Sims SD, Mann S (1996) *Chem Commun* 1367
25. Maciel GE, Bronnimann CE, Zeigler RC, Chuang IS, Kinney DR, Keiter EA (1994) In: Bergna HE (ed) *The colloid chemistry of silica*. American Chemical Society, Washington, DC, p 269
26. Fowler CE, Burkett SL, Mann S (1997) *Chem Commun* 1769
27. Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD (1998) *J Am Chem Soc* 120:6024
28. Lesaint C, Lebeau B, Marichal C, Patarin J (2005) *Microporous Mesoporous Mater* 83:76
29. King JF, Khemani KC (1989) *Can J Chem* 67:2162
30. Mbaraka IK, Shanks BH (2005) *J Catal* 229:365
31. Brinkmann U, Ettliger M, Kerner D, Schmoll R (2006) *Surfactant Sci Ser* 131:575
32. Tao T, Maciel GE (2000) *J Am Chem Soc* 122:3118
33. Siril PF, Cross HE, Brown DR (2008) *J Mol Catal A Chem* 279:63
34. Rosenholm JM, Czuryzskiewicz T, Kleitz F, Rosenholm JB, Linden M (2007) *Langmuir* 23:4315