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, N₂ adsorption/desorption, and solid-state ¹³C and ²⁹Si 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

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

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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$_2$SO$_4$, and H$_3$PO$_4$ 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$_2$)$_n$SH) may be attached to the silica framework via one, two, or three siloxane bonds. These T$_1$, T$_2$ and T$_3$ sites are readily distinguished by $^{29}$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$_1$ relative to T$_3$ 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$_2$ and T$_3$ sites, which tend to be more stable hydrothermally than T$_1$ 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 thioalkylsilane [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 α-fructose: the β-α-pyranose form is favored in water at room temperature, but the equilibrium shifts toward the β-α-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 Al₂O₃ columns. Toluene (Aldrich) was purified by passage through one column containing alumina and a second packed with CuO/Al₂O₃ (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 m²/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 readsorption 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 ¹³C and ²⁹Si, respectively. Samples were packed under an argon atmosphere into 4 mm zirconia rotors (Bruker). ²⁹Si cross-polarization/magic angle spinning (CP/MAS) spectra were obtained using a 90° pulse length of 3.00 μs, 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. ¹³C NMR (50.32 MHz, CDCl₃): δ 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). ¹³C NMR (50.32 MHz, CDCI₃): δ 50.00 (CH₂SO₃H), 30.83 (CH₃(CH₂)₂SO₃H), 30.66 ((CH₃)₂CH₂S), 29.66 ((CH₃)₂CH₂CH₂S), 24.16 (CH₂CH₂SO₃H), 21.16 (CH₂CH₂), 12.83 (CH₃)

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

Aerosil A380 (1.00 g) was dried by heating to 100 °C under vacuum (0.1 mTorr) for 12 h, then suspended in 50 mL toluene. MPTMS (400 μL, 2.05 mmol) was added and the mixture was refluxed for 15 h. The solid was washed with ethanol (3 x 15 mL), isolated by centrifugation, and dried at 100 °C under vacuum (0.1 mTorr) for 12 h. ¹³C CP/MAS NMR: δ 9 (Si(CH₃)₂), 27 (CH₂H₂SH), 50 (SiOCH₃). ²⁹Si CP/MAS NMR: δ -48 (T¹), -57 (T²), -100 (Q¹), -110 (Q²). Sulfur analysis: 1.16 wt%.

2.5 Installation of Propylsulfonic Acid Groups on Tp-A380

Tp-A380 (1.00 g) was transferred to a 100 mL two-necked round-bottomed flask under N₂. Dry THF (25 mL) was added and the flask was cooled to −78 °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 modified silica was dried at 100 °C under vacuum (0.1 mTorr) for 12 h. ¹³C CP/MAS NMR: δ 50 (CH₂SO₃H; SiOCH₃), 30 (CH₂H₂SH), 27 (CH₂H₂SH), 24 (CH₂CH₂SO₃H, SiCH₂CH₂), 11 (SiCH₂). ²⁹Si CP/MAS NMR: δ -48 (T¹), -57 (T²), -100 (Q¹), -110 (Q²). Sulfur analysis: 1.20 wt%.

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

To a 100 mL round-bottomed flask containing dry THF (25 mL), 1-butanol (500 μL, 4.67 mmol) was added under flowing N₂. After cooling to −78 °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 μL, 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 x 50 mL), followed by ethyl acetate (3 x 50 mL). The aqueous layer was acidified with 20 mL ethereal HCl (0.50 M) and washed with diethyl ether (2 x 20 mL). BTPSA was recovered as a viscous oil from the combined organic layers on a rotary evaporator (0.1 mTorr). ¹H NMR (200 MHz, CDCl₃): δ 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). ¹³C NMR (50.32 MHz, CDCl₃): δ 50.00 (CH₂SO₃H), 30.83 (CH₃(CH₂)₂SO₃H), 30.66 ((CH₃)₂CH₂S), 29.66 ((CH₃)₂CH₂CH₂S), 24.16 (CH₂CH₂SO₃H), 21.16 (CH₂CH₂), 12.83 (CH₃).
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 aqueous HCl (57.5 mL) and heated to 40 °C. P123 (2.00 g) was dissolved with stirring in 1.90 M aqueous HCl (57.5 mL) and heated to 40 °C. 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. 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 \(^{13}\)C CP/MAS NMR spectrum, Fig. 1a. The \(^{29}\)Si CP/MAS spectrum reveals monoalkylsilicon signals at –48 (T\(^1\)) and –57 ppm (T\(^2\)), Fig. 2a. The surface area and thiopropyl loading (inferred from sulfur analysis) are shown in Table 1.

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-butanol (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 \(^{13}\)C resonance of the sultone ring (69.9 ppm, CO) was not detected, implying that it had reacted completely. The characteristic \(C_s\) signal of 1-butanol, 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 \(^{13}\)C CP/MAS NMR spectrum, Fig. 1a. The \(^{29}\)Si CP/MAS spectrum reveals monoalkylsilicon signals at –48 (T\(^1\)) and –57 ppm (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 \(^{13}\)C CP/MAS NMR 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 \(^{29}\)Si CP/MAS NMR signal intensities are not quantitative, it is clear that the T\(^1\):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 T\(^1\) sites under the synthesis and/or workup conditions. The decrease in the Q\(^2\)/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...
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 $2\theta = 1.00^\circ$. N$_2$ adsorption/desorption gave a type IV isotherm characteristic of a mesoporous material (see Supplementary material).

The $^{13}$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 $^{29}$Si CP/MAS spectrum of the

![Fig. 1 Solid-state $^{13}$C CP/MAS NMR spectra for a Tp-A380; and b Taa-A380](image1.png)

![Fig. 2 Solid-state $^{29}$Si CP/MAS NMR spectra for a Tp-A380; and b Taa-A380](image2.png)

![Table 1 Physicochemical properties of supported catalysts](table1.png)
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 thiolpropyl groups do not appear to be present. In the $^{29}$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 thioalkyl-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 thiolpropyl-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 $^{13}$C CP/MAS NMR spectra for a Tp-SBA-15; and b Taa-SBA-15. Signals from the surfactant are denoted by asterisks](image)

![Fig. 4 Solid-state $^{29}$Si CP/MAS NMR spectra for a Tp-SBA-15; and b Taa-SBA-15](image)
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 (≥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 sulfone or sulfone.

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