FUNCTIONALIZED PERIODIC MESOPOROUS SILICA CATALYSTS FOR THE SELECTIVE DEHYDRATION OF CARBOHYDRATES


1 Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106
2 Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706
3 Department of Chemical Engineering, University of California, Santa Barbara, CA 93106

Introduction

Bioresnewable feedstocks are potential sources of carbon-neutral alternatives to fossil fuels. Specifically, 5-hydroxymethylfurfural (HMF) and its hydrogenated derivatives may be utilized as petroleum substitutes or additives, or as replacements for their derivatives. HMF is produced by dehydration of carbohydrates. Mineral acid catalysts show limited selectivity in complex solvent mixtures, and product separation is complicated.

Here we describe the incorporation of a new, bifunctional silane, 3-(3-trimethoxysilyl)propyl)thio)propane-1-sulfonic acid (TESAS), into SBA-15-type mesoporous ordered silica (MOS) by co-condensation. TESAS was designed as an acid dehydration catalyst for the conversion of fructose to HMF. Its thioether group may serve to promote selectivity to HMF, with or without oxidation to a sulfoxide or sulfone.

\[
\begin{align*}
\text{Me}_2\text{SiO} & \quad \text{O} \quad \text{Me} \\
\text{Me} & \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{OH} \\
\text{Me}_2\text{O} & \quad \text{Si} \\
\text{O} & \quad \text{Me} \\
\text{O} & \quad \text{Si} \\
\text{O} & \quad \text{O}
\end{align*}
\]

TESAS

A significant challenge in synthesizing a functionalized MOS is achieving a high loading of the functional group without loss of structural order. The functional groups in co-condensed silicas are more hydrothermally stable than grafted sites. However, to minimize structural defects created during functionalized MOS synthesis by co-condensation, the organosilanes have been restricted to functional derivatives of short alkyl chains (e.g., (3-mercaptop)trimethoxysilane, (3-aminopropyl)trimethoxysilane, APTMS). TESAS is considerably more complex than most co-condensed organosilanes previously used for pore surface functionalization, and changes in the synthetic procedure were required to achieve the desired product.

Experimental

Synthesis of TESAS-SBA-15. To prepare a mesoporous ordered SBA-15-type silica, Pluronic P123 (2.00 g) was dissolved with stirring in 1.6 M aqueous HCl (69 mL) and heated to 35 °C in a 250 mL HDPE bottle (Nalgene). TEOS (Si(OEt)\textsubscript{4}, 4.13 mL, 18.5 mmol) was added to the surfactant solution. Thirty minutes after introduction of TEOS, 425 mg NaCl (7.33 mmol, 0.10 M) was added to the reaction mixture. After 1 h, 700 mg of the Na\textsuperscript{+} salt of TESAS (2.06 mmol) was added in 44 mg increments every 15 min for 4 h. After 20 h, the reaction mixture was divided equally among three 30 mL Parr bombs with Teflon liners. Each was heated at 100 °C for 24 h. The resulting suspensions were filtered, washed with water and air-dried. The surfactant was removed by reflowing 1.30 g TESAS-SBA-15 in 500 mL of slightly acidified ethanol for 15 h. The solid was recovered by vacuum filtration and washed with 200 mL ethanol. The extraction process was performed once more on the filtrate. The resulting solid was washed with water and suspended in 100 mL 2 M HCl. After 3 h, the solid was collected and washed with water until the pH of the water was neutral. The solid was dried at 60 °C in air overnight, then at 150 °C under vacuum (0.1 mTorr) for 12 h.

Synthesis of SSA-SBA-15. TESAS may be oxidized at the thioether position during the synthesis of the modified SBA-15, resulting in a silica incorporating 3-(propylsulfonyl)sulfanylpropyl)propane-1-sulfonic acid (SSA) groups. To prepare SSA-SBA-15, the synthesis conditions for TESAS-SBA-15 were employed. After complete addition of TESAS, 4 equiv. aqueous H\textsubscript{2}O\textsubscript{2} (30 wt% 446 mL, 8.24 mmol) were added to the reaction mixture.

The identity and loading of TESAS and SSA groups were assessed by \textsuperscript{13}C CP/MAS and \textsuperscript{29}Si CP/MAS NMR spectroscopy, potentiometric titration, and elemental analysis. Pore structure and particle morphology were evaluated by N\textsubscript{2} porosimetry, TEM and powder XRD.

Catalytic Dehydration of Fructose. In a thick-walled glass reactor, 1.5 g of an aqueous layer consisting of 30 wt% fructose in deionized water and 3.0 g of an organic layer consisting of 7.3 (w/w) MBK-2-butanol were loaded with a catalyst and a triangular magnetic stirring bar. The reactors were sealed using Teflon liners inserted into plastic caps. An appropriate amount of catalyst was added to achieve a loading of 65 μmol acid, and the reaction time was adjusted to obtain approximately 80 % fructose conversion (judged visually). During reaction, the contents were stirred at 1000 rpm and heated at 130 °C, then cooled after reaction in an ethylene glycol-dry ice bath. The aqueous and organic layers were analyzed by HPLC. Fructose conversion was calculated as the moles of fructose reacted divided by the moles of fructose fed. HMF selectivity was calculated as the moles of HMF produced divided by the moles of fructose reacted.

Results and Discussion

Attempts to incorporate TESAS using established protocols for synthesizing organofunctionalized SBA-15 resulted in a nonordered silica. However, TESAS-SBA-15 was produced with two simple modifications to the synthesis procedure. First, NaCl was added 30 min after, rather than before, TEOS hydrolysis was initiated. Second, the addition of TESAS began 30 min later, and the organosilane was added slowly over 4 h. The \textsuperscript{13}C CP/MAS spectrum confirmed the presence of TESAS functional groups. The \textsuperscript{29}Si CP-MAS spectrum is typical of an organofunctionalized silica, in which the organosilanes are bound by two or three siloxane bonds (T\textsuperscript{2} and T\textsuperscript{3} sites) to the silica framework.

A reflection pattern typical of an ordered mesoporous material was observed by powder XRD. In addition to the d\textsubscript{002} reflection at 2θ = 0.80 °, the weak, broad reflection at ca. 1.6 ° is typical of organofunctionalized SBA-15. The 2-D hexagonal pattern of the mesopores was observed in the TEM images, Figure 1. The B.E.T. surface area (525 m\textsuperscript{2}/g) and pore diameter (4.7 nm) of TESAS-SBA-15 were obtained by N\textsubscript{2} adsorption/desorption, which yielded a type IV isotherm typical of mesoporous materials.
Conclusions

We have developed a solid, bifunctional acid catalyst containing a reaction promoter for the dehydration of fructose to HMF. It shows high selectivity at high conversion in a batch reactor test. However, when operated continuously under flow conditions, the catalyst deactivates over time. To improve its hydrothermal stability, catalyst modifications involving organic bisalkylated groups (e.g., 1,2-bis(trimethoxysilyl)ethane) are being explored.

Acknowledgement. The authors thank Dr. Se Gyu Jung for assistance in acquiring the TEM images. This work was supported by the NSF under the auspices of the Center for Enabling New Technologies through Catalysis (CENTIC). Portions of this work were made use of facilities of the Materials Research Laboratory, supported by the MRSEC Program of the National Science Foundation under award No. DMR05-20415.

References


Table 1. Dehydration of fructose to HMF a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass ng</th>
<th>Time min</th>
<th>Conversion %</th>
<th>Selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TESAS-SBA-15</td>
<td>142</td>
<td>141</td>
<td>84</td>
<td>71</td>
</tr>
<tr>
<td>SSA-SBA-15</td>
<td>82.0</td>
<td>140</td>
<td>81</td>
<td>65</td>
</tr>
<tr>
<td>Amberlyst 70</td>
<td>25.0</td>
<td>200</td>
<td>74</td>
<td>61</td>
</tr>
</tbody>
</table>

a The batch reactor contained the catalyst, 1.5 g aqueous fructose (30 wt%) and 3.0 g MBH/2-butanol (7.3 w/w). Reactions were conducted at 130 °C under autotomous pressure. Time was varied in order to achieve ca. 80 % conversion for each reaction.