

# Design of supported acid catalysts for the dehydration of alcohols

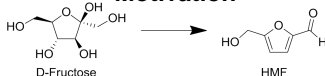


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## Motivation



Biomass-derived fuels and chemical intermediates may be renewable, eco-friendly alternatives to the world's dwindling fossil fuel reserves. Furans are an important class of chemical intermediate that could be produced from biomass through the dehydration of carbohydrates.<sup>1</sup> Specifically, 5-hydroxymethylfurfural (HMF) may serve as a substitute platform for the production of commodity chemicals and fuels. HMF has been synthesized with high selectivity (>80%) by homogeneous acid-catalyzed dehydration of fructose.<sup>2</sup> Unfortunately, that process requires a complex bi-phasic reaction system that includes a mineral acid catalyst (HCl) and a promoter (DMSO) in an aqueous phase, and an organic phase consisting of a mixture of methylisobutylketone and 2-butanol. We are developing an alternate system involving a heterogeneous catalyst to reduce or eliminate the need for the bi-phasic solvent system, by incorporating both acid and promoter functional groups onto a solid, porous substrate.

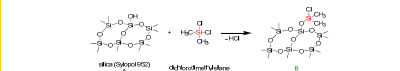
[1] Wepery T., Petersen, G. Top Value-Added Chemicals from Biomass: Volume 1: Results of Screening for Potential Candidates from Sugars and Synthesis Gas; US Department of Energy, 2004.  
[2] Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* 2006, 312, (5782), 1933-1937.

## First Generation Support: Preparation of Silica modified with Dehydration Reaction Promoter

We initially attempted to anchor a reaction promoter to a silica scaffold. DMSO was selected due to its ability to greatly enhance the selectivity for HMF production.

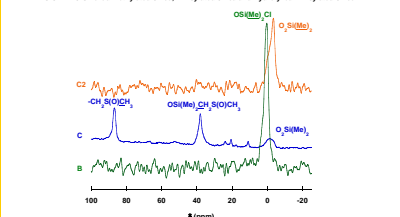
### Chlorination of Silica with Silylating Agent:

DMSO-functionalized silica was prepared in two steps. First, dichlorodimethylsilane was allowed to react with the surface hydroxyls to give  $\equiv\text{SiOSiMe}_2\text{Cl}$  groups.

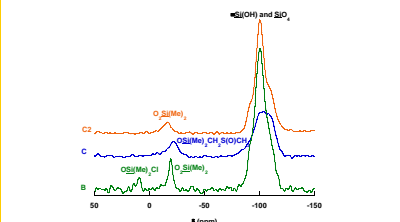


### Anchoring DMSO functionality:

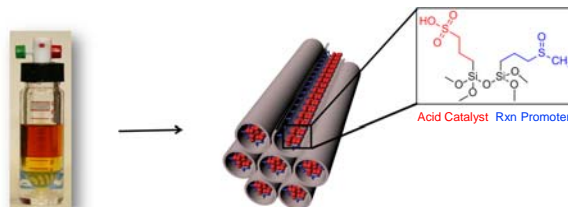
This modified silica was treated with dimethyl lithium to form  $\equiv\text{SiOSiMe}_2\text{CH}_2\text{S}(\text{O})\text{Me}$ .



<sup>13</sup>C CP-MAS Chloromethylated Silica, Dimethylated Silica and Hydrolyzed Dimethylated Silica



DMSO was successfully anchored to the silica but was found to be hydrolytically unstable.



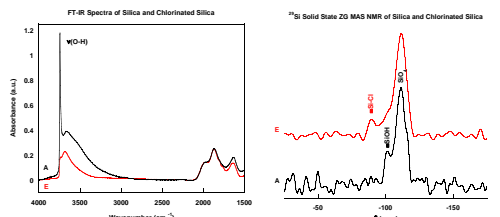
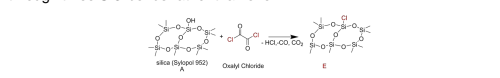
Our aim is to eliminate the complex biphasic dehydration system (left) in favor of a solid substrate with an anchored promoter and catalyst (right) for the production of 5-hydroxymethylfurfural from fructose.

## Second Generation Support: Alternate Promoter Functionalization of Silica

With the second generation materials, the hydrolytic stability was addressed.

### Direct Chlorination of Silica Support:

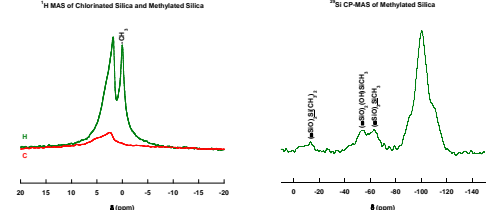
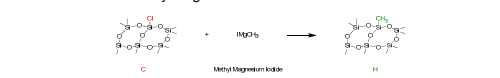
The silica was directly chlorinated with oxalyl chloride rather than using a silylating reagent. Thus the active chlorinated site should be anchored through three SiO bonds rather than one.



By FT-IR, the isolated O-H stretches from the silica disappear upon reaction with oxalyl chloride, which suggests -Cl replaces -OH. A Si-Cl signal is observed at -89 ppm in the single pulse <sup>29</sup>Si NMR spectrum. This chemical shift is consistent with DFT predictions.

### Methylation of Chlorinated Silica:

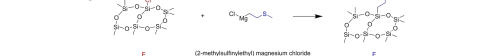
To demonstrate the reactivity of the chlorinated silica, the modified support was reacted with methylmagnesium iodide.



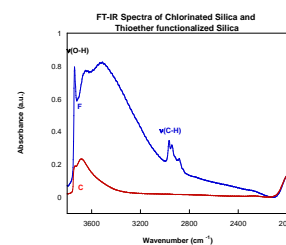
The silica was successfully methylated, as confirmed by solid state NMR.

### Thioether Alkylation of Chlorinated Silica:

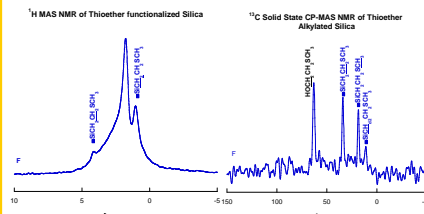
The chlorinated silica was reacted with a Grignard reagent, (2-methylsulfanyl)ethyl)magnesium chloride, to replace the chloride with a thioether functionality. The extra methylene group should increase stability of the linkage.



## Second Generation Support (cont'd):



The FT-IR spectrum shows the appearance of a C-H stretching mode after the reaction with thioether Grignard reagent.

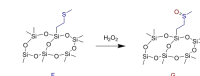


The existence of thioether functionalized silica was confirmed by solid state NMR.

However the quantity of functionalized sites appears to be low. Some of the linkages are thermally and hydrolytically stable.

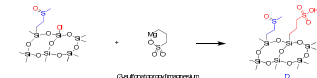
## Future Work

- Oxidize the sulfur to the sulfoxide



- Test the ability of the supported sulfoxide to promote the dehydration of 2-phenylethanol against soluble DMSO

- Increase acidity by anchoring sulfonic acid to the silica framework



## Conclusions

We have successfully

- Anchored DMSO to a silica support
- Developed an approach to directly chlorinating silica; resulting in a highly reactive support
- Formed a robust linkage between silica and a thioether by employing a Grignard reagent

Studies are underway towards enhancing the coverage of the thioether on silica. We are also analyzing the catalytic promotion by the oxidized thioether.

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