Selective Glucose Isomerization to Fructose Using A Heterogeneous Immobilized Tertiary Amines with Tuned Molecular Design

N.A. Brunelli,[a]* **N. Deshpande,**[a] **L. Pattanaik,**[a] **M. Whitaker**[a]
[a]*William G. Lowrie Department of Chemical and Biomolecular Engineering, Columbus, OH, 43210, USA*
**Corresponding author: Brunelli.2@osu.edu*

Abstract: The selective isomerization of glucose to fructose is investigated using immobilized tertiary amines. Highly active and selective catalysts are demonstrated. It is found that through changing the alkyl linker length to a methyl linker (C1) and increasing the organosilane loading to 1 mmol/g that high catalytic activity could be obtained. It was demonstrated through using the hot filtration test that the reaction does not proceed without the catalyst present. Finally, the C1 catalyst could be reused for multiple cycles while maintaining some catalytic activity.

Keywords: Tertiary Amine; Glucose Isomerization; SBA-15

1. Introduction

Biomass conversion has the potential to transform our ability to produce chemicals from renewable resources provided that challenges associated with catalytic selectivity can be overcome. Indeed, many biomass derived compounds originate from highly functionalized molecules such as cellulose that can be hydrolyzed to produce glucose. The key challenge is converting these highly substituted species into useful chemicals and intermediates such as 5-hydroxymethylfurfuraldehyde (HMF). A key step in this process is the isomerization of glucose to fructose. Commercial processes use enzymes to convert glucose to fructose, but this process requires maintaining highly controlled conditions not amenable for biomass processing.[1] Lewis acidic materials such as zeolite Sn-Beta have been investigated with promising results,[2,3] but these materials tend to be difficult to synthesize with crystallization times as long as 20 days being required.[4] Recent work has identified homogeneous tertiary amines as promising catalysts with similar selectivities as Sn-Beta.[5,6] Translating the interesting catalytic behavior of these tertiary amines to heterogeneous catalysts could overcome current limitations for selective isomerization of glucose to fructose. In this work, we will discuss our recent efforts to design heterogeneous catalysts with immobilized tertiary amines.

2. Experimental

All materials were synthesized and characterized using standard techniques, including NMR, N_2 physisorption, and CHN analysis.

Organic-Inorganic Composite Synthesis. SBA-15 are synthesized using standard methods.[7] All materials were calcined before grafting organosilanes onto the surface. We graft organosilanes with two different alkyl linker lengths (N,N-diethyl-amino-3-propyltriethoxysilane = C3 and N,N-diethyl-aminomethyltriethoxysilane = C1) on the surface of a high surface area mesoporous silica support.

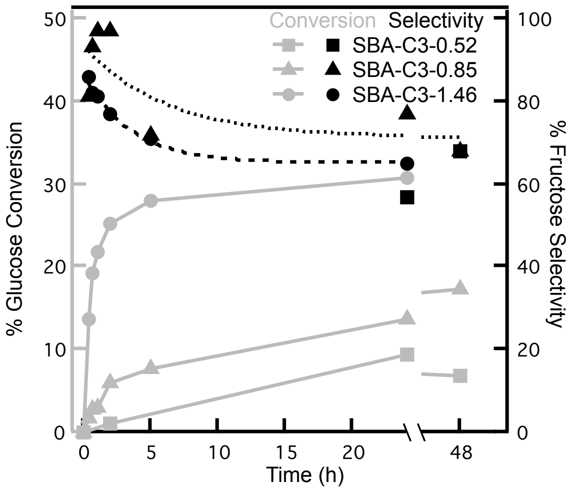

Figure 1. Comparison of catalytic conversion and selectivity of the isomerization of glucose to fructose using N,N-diethyl-amino-3-propyl functionalized on SBA-15 at three different loadings of 0.52 mmol N/g, 0.85 mmol N/g, and 1.46 mmol N/6. All reactions are performed using 10 mol% N (based on elemental analysis) using an initial glucose concentration of 10 wt% in water.

Catalytic Testing. The different silica composite materials are tested using 10 mol% N in the isomerization of glucose to fructose using an initial glucose concentration of 10 wt% and a reaction temperature of . The conversion and selectivity are determined through analyzing with HPLC samples taken at different time points to determine conversion and selectivity.

Catalyst Reuse Testing. The catalytic materials are reused through collecting the catalyst after reaction through using filtration. The catalyst are characterized and reused to determine conversion over time in a second round of catalytic testing.

3. Results & Discussion

All materials are characterized using standard techniques. The characterization data is described in a recent publication.[8] The catalytic activity for the materials is evaluated through determining the conversion of glucose and the yield of fructose after fixed times. Initial catalyst testing is performed using a mesorporous silica grafted with N,N'-diethyl-amino-3-propyl organosilane (C3) with a loading of 0.52 mmol N/g. This catalyst with low amine coverage had low catalytic activity, achieving a conversion of 18% after 24 hours, as shown in Figure 1. Experiments with homogeneous triethylamine and mesoporous silica indicated that the presence of silanols reduced the catalytic activity of tertiary amines. Therefore, this limitation is overcome through increasing the grafting density of the amine on the silica surface. With increased organosilane loading, the catalytic activity increases with the highest catalytic activity being observed for the C3 organosilane at a loading of 1.46 mmol N/g. Interestingly, higher conversion and selectivity could be obtained when performing this reaction under nitrogen (not shown).

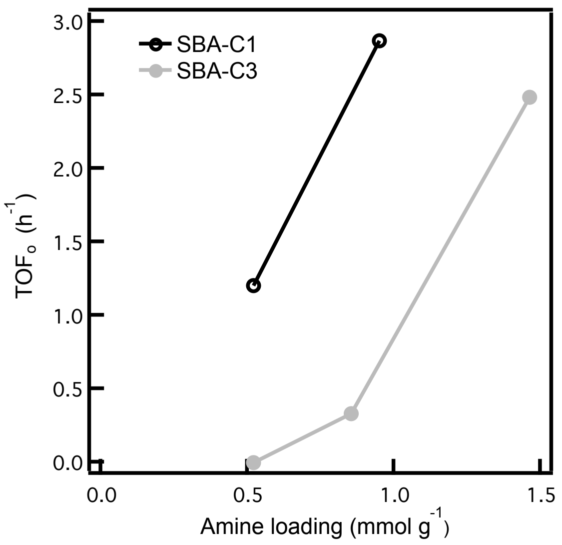

Figure 2. Comparison of the initial turnover frequency for tertiary amine organosilanes with different linker lengths functionalized at different densities on the surface of SBA-15.

While increasing the loading can help mitigate amine silanol interactions, an alternative method to limit amine-silanol interactions is investigated that involves reducing the organosilane linker length. Indeed, previous work should that tuning the alkyl linker length could impact the catalytic activity by an order of magnitude change in initial turnover frequency (TOF_0). Through grating the N,N-diethyl-aminomethyl (C1) organosilane on the same silica surface, a catalyst with limited to no amine-silanol interactions is obtained. Catalytic testing reveals that the catalytic material with the C1 organosilane has higher catalytic activity than a catalytic material with the C3 organosilane at similar loading, as shown in Figure 2.

Additional work examines the ability to reuse these different catalytic materials. For the C3 catalyst, the catalyst tends to deactivate by both leaching of the organosilane and irreversible deactivation of the tertiary amine. While the C3 organosilane material deactivates almost completely, the C1 material retains a greater amount of the overall catalytic activity. While losing some organosilane to leaching, the C1 catalyst remains active for the glucose isomerization to fructose. These promising results demonstrate that sustainable biomass conversion is indeed possible and provide insights on how to design an effective catalyst for the key step of glucose isomerization.

4. Conclusions

The molecular design of the catalytic material impacts the catalytic activity and reusability. Through synthesizing, characterizing, and testing a series of catalytic materials, it is found that silanols can limit catalytic activity of immobilized tertiary amines. These activity challenges can be overcome through tuning the molecular design of the catalyst. Through using a catalyst with an alkyl linker (C1), it is found that higher catalytic activity can be obtained. The C1 catalyst also can be recycled more efficiently than a C3 catalyst with similar loading since the C1 catalyst does not undergo irreversible deactivation.

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