Journal of Catalysis 353 (2017) 205–210

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Selectively converting glucose to fructose using immobilized tertiary amines

Nitish Deshpande, Lagnajit Pattanaik, Mariah R. Whitaker, Chi-Ta Yang, Li-Chiang Lin, Nicholas A. Brunelli *

The Ohio State University, William G. Lowrie Department of Chemical and Biomolecular Engineering, 151 W. Woodruff Ave., Columbus, OH 43210, United States

ARTICLE INFO

Article history:
Received 18 May 2017
Revised 20 July 2017
Accepted 20 July 2017
Available online 7 August 2017

Keywords:
Biomass
Glucose isomerization
Linker length
Aminosilica materials

ABSTRACT

Glucose isomerization to fructose is an important step in upgrading biomass to higher valued products. Tertiary amines can be highly selective catalysts for this reaction. In this work, tertiary amine analogues were functionalized on a mesoporous silica support to create heterogeneous catalytic materials. Experiments with homogeneous catalysts and silica revealed that silanols reduced the catalytic activity. Through using different strategies to limit amine-silanol interactions, it is determined that tuning parameters such as amine loading and alkyl linker length of the amine tether increases the fructose yield by a factor of four. Among the catalysts tested, the one found to be the best for glucose isomerization has a high amine loading ($\sim$0.95 mmol g^{-1}) with a methyl linker. Catalyst reuse tests demonstrated that organosilane leaching reduced amine content, but the immobilized amines with the methyl linker retained greater catalytic activity than amines with propyl linkers.

1. Introduction

Catalytic material design is critical for enhancing catalyst activity and selectivity. Indeed, the precisely designed catalyst can enhance activity by an order of magnitude [1,2] and improve catalytic selectivity [3]. While many design discoveries have been made for homogeneous catalysts, it is desirable to translate these discoveries to heterogeneous catalytic materials since these can be more easily separated from the reaction mixture to yield the desired product, making the process more environmentally friendly. Translating these discoveries to heterogeneous catalytic materials presents a considerable challenge since heterogeneous catalytic materials often are non-uniform and present other complications. Therefore, additional research is necessary to investigate these design challenges and identify methods to ensure high catalytic activity and selectivity.

Identifying design features that can increase catalytic activity and selectivity is particularly important for biomass related reactions such as the isomerization of glucose to fructose. Interest in this reaction has greatly expanded with the discovery that the Lewis acidic catalyst Sn-BEA can selectively convert glucose to fructose [4]. The unprecedented results for Sn-BEA have produced numerous investigations that create a more detailed understanding of the catalytic process, but the performance remains limited for Sn-BEA since it has been demonstrated that the catalyst deactivates [5] presumably through leaching of Sn active sites from the catalyst [6]. Therefore, alternative catalysts have been investigated, including recent work examining base catalyzed reactions [7–9]. The base catalyzed method was thought to be poorly selective since inorganic bases tended to give low yields and selectivities [10–13]. However, recent work with organic bases such as triethylamine demonstrates that catalytic materials using base can offer a viable route for fructose production [7]. The most selective organic base catalyst was a tertiary amine. The current understanding is that tertiary amines serve to create a hydroxide ion that is thought to be responsible for the catalytic activity.

These homogeneous catalytic results provide a basis for creating heterogeneous catalytic materials that can be separated from the reaction mixture, facilitating product purification. Recent work on catalyst immobilization have targeted polymers [14] and magnetic nanoparticles [15], finding good yields from the heterogeneous catalysts. Magnetic nanoparticles are intriguing because of the facile separation process, but these tend to be utilized for specialty applications rather than bulk chemical processing because of current costs. Organic polymers and mesoporous silicas often provide complementary strategies for catalyst immobilization. Polymers can have higher loadings, but can have complex solvent and temperature dependent phase behavior that introduce mass-transfer limitations to the system and limit the accessibility of catalytic sites. Mesoporous silica has a rigid backbone that creates

---

* Corresponding author.
E-mail address: Brunelli.2@osu.edu (N.A. Brunelli).
@OSUChemEProfBru (N.A. Brunelli)

http://dx.doi.org/10.1016/j.jcat.2017.07.021
0021-9517/© 2017 Elsevier Inc. All rights reserved.

uniform pores that facilitate access to the catalytic sites. The improved mass transfer comes with the disadvantage that the organosilanes can leach, which can be catalyzed by basic organosilanes [16]. While typical organosilanes have a propyl linker and attach to the silica surface on average via a bipodal manner (two attachment points) [17], recent work investigating the effect of alkyl linker length on reaction rates found that an aminosilane containing a methyl linker between the nitrogen and silicon atom was found to attach *via* a tripodal attachment [18]. The increased number of attachment points would potentially increase the stability. Simultaneously, a methyl linker may limit the ability of the amine to catalyze the siloxy bond cleavage, limiting the overall amount of leaching.

Herein is described work to investigate a series of mesoporous silica catalytic materials containing tertiary amines for the isomerization of glucose to fructose (Fig. 1). Investigations focused on the effect of the loading and the alkyl linker length of the organosilane on catalytic performance. The materials are also investigated in catalytic recycle experiments to understand the nature of deactivation. Overall, the work demonstrates the importance of catalytic material design to increase catalyst performance.

2. Experimental methods

2.1. Chemicals

All chemicals were used as received with no further purification with the exception of toluene. Toluene (ACS grade, Macron Fine Chemicals) was dried using an MB-SPS DriSolv system (MBraun Inc.). The following chemicals were used tetraethylorthosilicate (98%, Acros Organics), hydrochloric acid (36.5–38.0% by wt., reagent grade, J. T. Baker), poly(ethylene glycol)-block-poly (propylene glycol)-block-poly(ethylene glycol) PEG-PPG-PEG, Pluronic® P-123 (Sigma-Aldrich), hexamethyldisilazane (>99%, Sigma-Aldrich), (N,N-diethylaminomethyl) triethoxysilane (Gelest), (N,N-diethyl-3-aminopropyl) trimethoxysilane (Gelest), hexanes (ACS grade, Macron Fine Chemicals), *d*extrose (USP grade, Fisher), *D*-(+)-mannose (99%, Alfa Aesar), *D*-fructose (99%, Alfa Aesar), D-mannitol (USP grade, Amresco), dimethylsulfoxide (>99.5%, Sigma-Aldrich), acetonitrile (>99.9%, VWR Analytical), tetrahydrofuran (>99.9%, Fisher Scientific, HPLC grade), and reagent alcohol (BDH VWR Analytical). De-Ionized (DI) water was obtained from a house supply that produces Milli-Q quality water.

2.2. Catalyst synthesis

Pure silica SBA-15 was synthesized using procedures reported in literature [19,20]. Organosilanes with tertiary amine functionality were immobilized onto this SBA-15 using methods reported in literature [19]. The organosilanes that were separately grafted on silica surface were (N,N-diethyl-3-aminopropyl) trimethoxysilane (C3) and (N,N-diethylaminomethyl) triethoxy silane (C1). The convention used for naming the materials involved the organosilane linker length (C1 vs. C3) and the actual loading. For a material functionalized with C3 and an actual loading of 0.52 mmol g^{-1}, the material was labeled SBA-C3-0.52. Materials capped with hexamethyldisilazane (HMDS) were labeled according to its tertiary amine type and loading with "-HMDS" as a suffix.

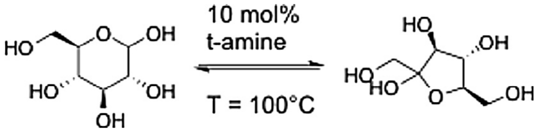

Fig. 1. Tertiary amine catalyzed glucose isomerization to fructose.

2.3. Material characterization

The materials were characterized using a battery of standard techniques, including nitrogen physisorption, thermo-gravimetric analysis with differential scanning calorimetry (TGA-DSC), elemental (CHN) analysis, and ^{29}Si CP/MAS NMR. The textural properties of the materials were analyzed using Micromeritics 3Flex surface characterization analyzer. All samples display type (IV) adsorption-desorption isotherms, consistent with isotherm behavior for mesoporous materials like SBA-15. The surface area and pore volume were calculated using the BET method while the pore size was determined using the BdB-FHH method [21]. Data for all materials is presented on a per gram of silica basis that was determined through accounting for organic content from TGA. TGA-DSC were performed using STA 449 *F5 Jupiter*® (NETZSCH instruments). Analysis was performed under flowing air (20 mL/min) and nitrogen (20 mL/min) at a ramp rate of 10°C/min from 30°C to 900°C followed by a 5 min hold at 900°C. Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA) on all the samples to determine the weight percentages of carbon, hydrogen, and nitrogen in the functionalized samples. The weight percentage of nitrogen was used to calculate the loading of organosilane functionalized onto the catalysts. Solid-state ^{29}Si CP/MAS NMR experiments were performed using Bruker DSX 300 MHz spectrometer operating at 59.6 MHz for ^{29}Si. (3-(trimethylsilyl)-1-propanesulfonic acid sodium salt) is used as the chemical shift reference (0 ppm). Experimental parameters included magic angle spinning at 5 kHz, a cross-polarization time of 5 ms, relaxation delay of 2 s, and ^{1}H decoupling at $\sim$90 kHz.

2.4. Catalytic testing - Kinetic evaluation

Isomerization reactions were carried out in 15 mL glass pressure tubes equipped with magnetic Teflon stir bars (VWR). These pressure tubes were heated in a silicone oil bath using a digital temperature-controlled stirring hot plate (Heidolph). A bulk reaction solution consisting of 4.0 g dextrose and 36.0 g DI water was prepared. Two grams of this solution were combined with an amount of the catalyst to achieve an equivalent amount of amine loading of 10 mol%. The pressure tube was sealed using a Teflon cap equipped with a back-sealing O-ring and placed in a preheated (100°C) oil bath for fixed intervals of time. The reaction was quenched by placing the reactor in an ice bath for 15 min. Weighing the pressure tubes before and after the reaction showed no loss of its contents. The reaction mixture was diluted with 4 g of 0.3 M d-mannitol solution (internal standard for HPLC measurements). The pressure tube was closed and shaken vigorously before taking a 1.8 mL sample using disposable syringes. The sample was then filtered using a 0.22 µm nylon (∅ = 13 mm) syringe filter and analyzed using High Performance Liquid Chromatography (HPLC) from Waters (Acquity) equipped with a refractive index (RI) detector. Glucose, fructose, and mannitol concentrations were monitored using Waters Sugar Pak-1 column equipped with a precolumn filter. DI water was used as the mobile phase at a flow rate of 0.20 mL/min and a column temperature of 70°C. Using the Weisz-Prater criteria and varying the stirring speed to examine mass transfer limitations at the reaction conditions, it can be concluded that mass transfer effects did not affect the results (Tables S8 and S9). For reactions under nitrogen, a similar procedure was followed, except the reaction was performed in a Schlenk tube and the reaction mixture was degassed using freeze (liquid nitrogen)-thaw cycles (4 times). To understand how the solution