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Methyl-ligated tin silsesquioxane catalyzed reactions of glucose

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ABSTRACT

Tin-containing zeolite Beta (Sn-Beta) has been investigated as a catalyst for isomerizing aldohexoses into ketohexoses through a Lewis acid mediated hydride shift. Recent studies on the reactivities of Lewis base-doped and alkali-exchanged Sn-Beta samples have conclusively demonstrated that the "open" tin site performs the glucose isomerization reaction. With Lewis base doped Sn-Beta, glucose conversion is almost completely eliminated and product selectivity is shifted predominantly to mannose. These data suggest that glucose reactions may occur through pathways that do not involve the "open" site in Sn-Beta; albeit at significantly lower rates. To examine this possibility, reactions of glucose catalyzed by a homogeneous model of Sn-Beta that does not contain "open" sites, methyl-ligated tin silsesquioxane **1a**, is experimentally and theoretically examined. **1a** is an active glucose conversion catalyst selectively producing mannose, although the rates of reaction are far below those obtained from Sn-Beta. A hybrid quantum mechanical/molecular mechanics model is constructed, and the complete catalytic cycle is computationally examined, considering ring-opening, three distinct pathways for each hydride- and carbon-shift reaction, and ring-closing. The combined experimental and computational results suggest that there could be reaction pathways that involve Si–O–Sn cleavage that give much slower reaction rates than the open tin site in Sn-Beta.

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1. Introduction

Microporous solids containing Lewis acid sites have garnered considerable interest for their ability to selectively convert highly functionalized, carbonyl-containing molecules such as glucose [1–3]. Interest in carbonyl-based chemistry has been driven by the attractiveness of producing transportation fuels and fine chemicals from biomass-derived sources [4–6]. A tin-containing molecular sieve with the zeolite beta topology (Sn-Beta) has emerged as a useful solid Lewis acid catalyst to perform highly selective reactions with carbohydrates, such as the isomerization of glucose to fructose [7]. Sn-Beta, initially synthesized by Corma et al. [8,9], has been demonstrated to catalyze the Baeyer-Villiger oxidation of ketones to lactones [9,10], Meerwein-Ponndorf-Verley (MPV) reduction of aldehydes and ketones [11,12], epimerization of glucose [13–16], carbon–carbon bond coupling reactions [17,18], and Diels-Alder reactions [19].

The efficacy of Sn-Beta has stimulated research on resolving the active catalytic site and mechanism for the glucose isomerization reaction. Metal-containing zeolites like Sn-Beta, contain a distribution of "closed" sites (a $(SiO)_4Sn$ center) and "open" sites (a $(SiO)_3$-SnOH center with an adjacent silanol group) that occur when the framework is partially hydrolyzed [20]. In a recent study, Harris et al. demonstrated that the number of open and closed sites in Sn-Beta may be quantitatively determined utilizing Lewis bases as titrants [21]. In the same report, an inverse linear correlation between the initial rate of glucose isomerization with the amount of pyridine dosed was demonstrated, implying that isomerization activity should be fully suppressed when all open sites are titrated. Bermejo-Deval et al. sodium-exchanged the silanol groups adjacent to the open tin site and observed a complete shift in selectivity from fructose to mannose, providing the first experimental evidence that the open site was the most active tin site, as well as emphasizing the significance of the silanol moiety in the reaction mechanism [16]. This work also revealed that titration of the open site with NH_3 (Sn-Beta-NH_3) attenuated the activity of the catalyst indicating that the open and closed sites do not interconvert under reaction conditions.

Several different reaction mechanisms involving a catalytically active open site have been proposed. Work from Li et al. [22] suggests that glucose first binds to the open site through coordination

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of the basic C_1 carbon hydroxyl, with subsequent transfer of the acidic proton to the framework lattice followed by a 1,2-intramolecular hydride shift. This results in a monodentately bound fructose stabilized by the adjacent silanol group through the O_1 oxygen. Yang et al. [23] consider a similar type of mechanism involving the closed site. Rai et al. [24] and Christianson et al. [25] propose similar pathways, however, their calculations involve the acidic C_2 hydroxyl proton transferring to the stannanol group, forming a water molecule. Rai et al. also demonstrated that in the absence of a silanol group adjacent to the tin center, the glucose binds to the tin bidentately and selectively produces mannose through a 1,2-intramolecular carbon shift. Experimental results support this prediction [16]. The Davis Lab has also shown the effect of the silanol moiety in directing the selectivity of glucose conversion to either fructose or mannose using a pair of silsesquioxanes retaining an octahedral tin site with and without an adjacent silanol substituent [26].

The observation of some glucose activity despite poisoning (Sn-Beta-NH_3) implies that there may be other reaction pathways with rates slower than those catalyzed by the open site in Sn-Beta. One possible pathway could involve the protonation of a framework Sn–O–Si bond by glucose to facilitate binding to the Lewis acidic site. To test this case, we synthesized a methyl-ligated tin silsesquioxane (**1a**), and investigated its glucose reaction pathways, both experimentally and theoretically. Compound **1a** contains a tin atom terdentately bound to a silsesquioxane ligand through three Sn–O–Si bridging bonds, as schematically shown in Fig. 1. Here, we demonstrate that **1a** is an active catalyst (but with low rates of reaction) for the conversion of glucose to mannose and fructose *via* 1,2-intramolecular carbon and hydride shifts, respectively. Additionally, a hybrid quantum mechanics/molecular mechanics (QM/MM) electronic structure model is used to compare pathways in the production of fructose and mannose. The catalytic cycle model consists of three distinct operations: (1) deprotonation and ring-opening of glucose, (2) hydride- or carbon-shift (Bílik) reactions, and (3) ring-closing and reprotonation of the mannose or fructose products.

2. Experimental methods

All glassware was dried at 433 K prior to all syntheses, and purged with argon while cooling. All syntheses, purification procedures, and reaction tests were carried out under argon using standard air- and water-free techniques. Benzene (99.8%, anhydrous, Sigma-Aldrich), hexane (95%, anhydrous, Sigma-Aldrich), tetrahydrofuran (THF, ⩾99.9%, anhydrous, Sigma-Aldrich), dimethyl sulfoxide (DMSO, ⩾99.9%, anhydrous, Sigma-Aldrich) and acetonitrile (99.8%, anhydrous, Sigma-Aldrich) were used as received. Triethylamine (99.5%, Sigma-Aldrich) was distilled from 3A molecular sieves. Methyltin trichloride (97%, Sigma-Aldrich) was used without further purification. Heptacyclohexyl trisilanol silsesquioxane (**1**) was obtained from Hybrid Plastics and recrystallized by slow diffusion of acetonitrile into a concentrated THF solution; its purity was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR [27].

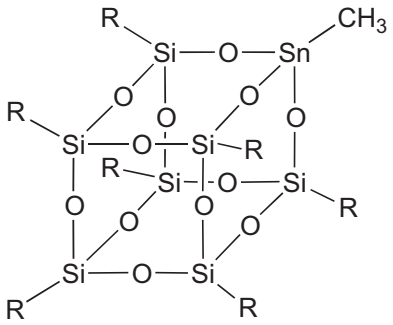

Fig. 1. Schematic representation of the structure of **1a**. R = cyclohexyl.

2.1. Synthesis of *1a*

1a was synthesized by the reaction of methyltin trichloride with the incompletely condensed trisilanol silsesquioxane **1**, as reported by Feher et al. [27] To ensure that all triethylamine (used as a scavenger base, and reported to be a highly selective catalyst in the conversion of glucose to fructose [28]) was removed from the product, acetonitrile was layered onto a concentrated solution of **1a** in benzene. The resultant white powder was filtered and dried for 12 h under a dynamic vacuum of <50 mTorr.

2.2. Material characterization

Nuclear magnetic resonance (NMR) spectra of **1a** were collected either on a Varian Inova 500 (^{1}H, 499.7; ^{13}C, 125.7 MHz) equipped with a broadband probe or on a Varian Inova 400 (^{29}Si, 79.4; ^{119}Sn, 149.1 MHz). ^{29}Si and ^{119}Sn NMR were referenced to $SiMe_4$ and $SnMe_4$, respectively. Chromium(III) acetylacetonate ($Cr(acac)_3$) was added to samples for ^{29}Si and ^{119}Sn NMR characterization as a shiftless relaxation agent.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 1.60–1.90 (vbr m, 35 H, CH_2), 1.10–1.33 (vbr m, 35 H, CH_2), 0.94 (s, 3 H, CH_3), 0.65–0.81 (vbr m, 7 H, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): 27.70, 27.56, 27.18, 26.95, 26.73, 26.67 (s, CH_2); 24.35, 23.44, 23.24 (s, 3:3:1 for CH); −3.13 (s, CH_3). ^{29}Si NMR (79.4 MHz, $CDCl_3$, 298 K, 0.02 M Cr(acac)$_3$): −65.01, −68.24, −69.55 (s, 3:1:3). ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 298 K, 0.02 M $Cr(acac)_3$): −247.60.

2.3. Reaction procedures

Reactions of D-glucose (Sigma-Aldrich, anhydrous, ⩾99.5%) were conducted under anhydrous conditions in 10 mL thick-walled glass reactors (VWR) that were heated in a temperature-controlled oil bath placed on top of a digital stirring hot plate (Fisher Scientific). Both glucose and **1a** were separately dried under vacuum (<50 mTorr) for at least 12 h prior to the addition of anhydrous DMSO and benzene solvents, respectively. Glass reactors (with their stir bars) were dried for at least 3 h at 433 K, capped with Teflon septa, and purged with argon while cooling. In a typical reaction, the dried reactors were charged with 6 mL of a 1:1 volumetric ratio of the catalyst and glucose stock solutions, resulting in a 2% (w/w) initial glucose solution, with a glucose:Sn molar ratio of 75. Reactors were placed in the oil bath at a predetermined temperature, and approximately 125 mg aliquots were extracted at regular time intervals. These reaction aliquots were mixed with 125 mg of a 2% (w/w) aqueous D-mannitol (Sigma-Aldrich, ⩾98%) solution, which was used as an internal standard for quantification. To ensure thorough catalyst removal from the aliquot solution prior to quantification, 0.3 mL of H_2O was added, and the solution was filtered using a 0.2 μm PTFE syringe filter.

Reaction aliquots were analyzed by high performance liquid chromatography (HPLC) using an Agilent 1200 system (Agilent) equipped with refractive index (RI) and evaporative light scattering (ELS) detectors. The glucose, fructose, mannose, and mannitol fractions were separated with a Hi-Plex Ca column (6.5 × 300 mm, 8 μm particle size, Agilent) held at 353 K. Ultrapure water was used as the mobile phase at a flow rate of 0.6 mL min^{-1}.

Glucose conversion and product yields were calculated by

$$X_{Gluc}(t) = \frac{n_{Gluc}(t=0) - n_{Gluc}(t)}{n_{Gluc}(t=0)} \times 100\ [\%]$$

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