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Beyond tin-containing zeolites ? New opportunities in catalytic carbohydrate conversion by Tin-Organic Frameworks

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PURPOSE OF THE ABSTRACT

Lewis acid catalysts normally undergo deactivation in aqueous media. A few examples of water-tolerant Lewis acid catalysts, such as Ti-beta zeolite for Baeyer-Villiger oxidation or Sn-beta zeolite for glucose-fructose isomerization, are nevertheless known. The active sites of these catalysts present isolated metal cations embedded into a matrix of silicalite. Hydrophobicity of the silicalite network protects the Lewis acidic centers from hydrolysis, whereas an organic substrate easily interacts with them [1]. Inspired by examples of zeolites, we synthesized porous tin-organic frameworks (Sn-OF) as potentially water-tolerant materials bearing Lewis acidic sites [2]. The Sn-OFs were tested for isomerization of glucose into fructose [3,4], as this reaction is well-known for tin cations embedded into a network of a silicalite zeolite (Sn-beta).

Unexpectedly, mannose (an epimer of glucose) appeared to be the main product of the isomerization over the Sn-OFs. Screening of the temperature, reaction time, and solvent (an H₂O-EtOH mixture with water content of 50-100 wt%) revealed that mannose remains the main isomerization product in the presence of the Sn-OFs under the broad range of applied reaction conditions. At the same time, fructose always predominates upon glucose isomerization over Sn-Beta zeolites. Filtration test supported that the Sn-OFs heterogeneously catalyze the reaction. We also studied isomerization of other similar monosaccharides. In all the cases the Sn-OFs mainly catalyze the epimerization at C-2 position of aldoses. The mechanism of the glucose isomerization was investigated using D-(1-¹³C)-glucose as a substrate. D-(2-¹³C)-mannose was obtained as a product, suggesting a carbon skeleton rearrangement, i.e., breaking of a C-2/C-3 carbon bond and formation of a C-1/C-3 bond. Hence, an epimerization mechanism was suggested based on the following steps: The initial step is the protonation of the Sn-OH group with the proton from the OH-group attached to C-2 (a) followed by a bidentate coordination of glucose at the tin site (b). This transition state (c) enables the carbon shift of C-3 bound to C-2 towards the formation of a new C-C bond with the initial C-1 carbon. Finally, the formed epimeric aldose is desorbed and replaced again by the initial hydroxyl group resulting in a closed catalytic cycle. To obtain a deeper insight into a structure of active sites of the Sn-OFs, tetraphenyltin and triphenyltin hydroxide were tested as model molecular catalysts. The former shows no catalytic activity, while the latter catalyzes glucose epimerization into mannose with 78% selectivity. This result highlights the catalytic significance of partially hydrolyzed tin sites with an attached hydroxyl group. Furthermore, the basicity of this hydroxyl group is crucial for catalysis, since the reaction rate dramatically decreases in acidic medium. However, the catalyst remains highly active and selective under proper treatment.

In conclusion, we report an unexpected catalytic activity of Sn-OFs as solid catalyst for selective epimerization of aldoses. Catalytic performance of Sn-OFs is determined by (1) Lewis acidity of tin; (2) free Sn-OH groups; and (3) the high hydrophobicity of organic linkers. Thus, it is shown that beyond conventional zeolite catalysis novel classes of materials pose great potential for the conversion of biogenic platform chemicals especially considering reactions that prefer an aqueous environment. Not only novel conversion routes for carbohydrates have been made accessible but also the application of Sn-OFs enables carbon-efficient synthesis of rare monosaccharides [3, 4].

[2] J. Fritsch, M. Rose, P. Wollmann, W. Böhlmann, S. Kaskel, *Materials* 2010, 3, 2447-2462.

[3] M. Rose, I. Delidovich, R. Palkovits, Patent application DE 10 2016 116 121.7.

[4] I. Delidovich, A. Hoffmann, A. Willms, M. Rose, *ACS Catal.* 2017, 7, 3792-3798.

FIGURES

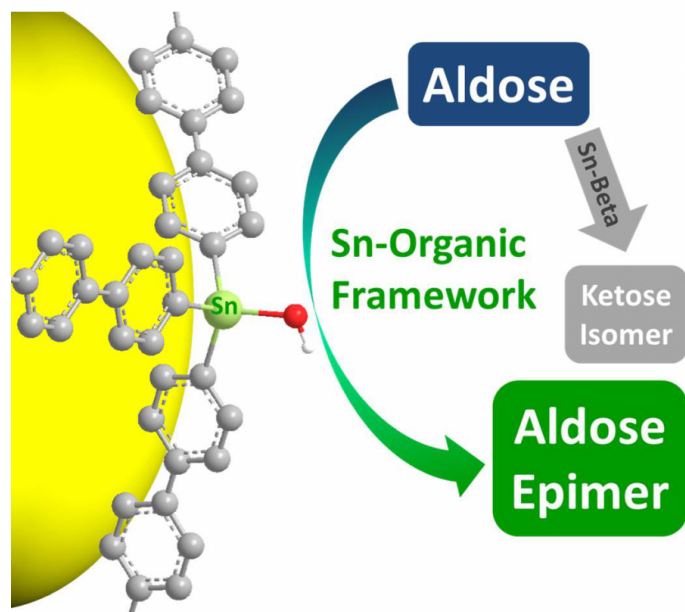


FIGURE 1

Tin-organic-framework as novel solid catalyst
Epimerization reaction of aldoses instead of
isomerization using Sn-beta zeolite

FIGURE 2

KEYWORDS

organic framework | sugar isomerization | tin catalyst | heterogeneous catalysis

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