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Porous Tin-Organic Frameworks as Selective Epimerization Catalysts in Aqueous Solutions

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PURPOSE OF THE ABSTRACT

Nowadays, the interest to biomass valorization in technological areas such as chemical, fuel and food industry is rapidly increasing. In this regard, the conversion of carbohydrates as the most readily available terrestrial biomass components is of utmost importance. [1] As the number of abundant monosaccharides in nature is only limited to seven, the focus is placed on the synthesis of rare monosaccharides, which exhibit interesting and unique properties. [2] The epimerization products, L-ribose, D-lyxose, L-quinovose, and D-talose belong to the group of rare monosaccharides with great application potential in medical and pharmaceutical industry. L-ribose is of utmost interest as starting agent for synthesis of drugs for the treatment of the Hepatitis B Virus and the Epstein-Barr-Virus.[3] D-talose serves as starting agent for manufacturing of antitumor drugs.[4] In spite of the extremely high interest towards application of rare saccharides in different fields, a high price of these compounds significantly restricts their utilization even in laboratory scale. Consequently, development of novel synthetic methods for efficient production of rare monosaccharides are required.

Element-organic frameworks are a young class of nanoporous inorganic-organic hybrid materials and offer high potential in heterogeneous catalysis for the conversion of carbohydrates. Recently, catalytic activity for epimerization of monosaccharides of Lewis acidic porous tin-organic frameworks (Sn-OF) was uncovered. The Sn-OFs demonstrated outstanding epimerization selectivity for the following pairs of monosaccharides: glucose-mannose, ribose-arabinose, and xylose-lyxose.[5]

The tin-organic frameworks, Sn-OF-1 and Sn-OF-2, were synthesized using organolithium chemistry as shown in Figure 1. First, a nucleophilic aryl lithium intermediate is formed which is then crosslinked by the addition of a tin-based precursor (Figure 1). The catalysts were characterized by N2 physisorption and IR spectroscopy. The materials exhibit high surface areas of 350 m2·g-1 for Sn-OF-1 and 506 m2·g-1 for Sn-OF-2. The catalytic tests were performed using 10 wt.% monosaccharide solutions in 50 wt.% ethanol: 50 wt.% water. The conversion for Sn-OF-1 was in the range of 12-36 % with a selectivity for the epimerization product of 77-90% at 100 °C after 1.5 h. The yield for the epimeric aldoses reached 20-25%with only 2-5% of the corresponding ketose (Figure 2). The mechanism was investigated, and the structure of the catalytically actie sites was deduced. The combination of partially hydrolyzed Sn-sites covalently connected by organic aromatic linkers and highly hydrophobic confined pore spaces was suggested to lead to outstanding selectivity for the epimerization reaction. Moreover, it was shown that the hydroxyl groups attached to the Sn-sites have a catalytic significance. Tetraphenyltin showed no catalytic activity compared to triphenyltin hydroxide which led up to 70 and 10% selectivity for mannose and fructose. Furthermore, it was proven by filtration test that the catalysts exhibit no leaching of Sn during the reaction. By isotope exchange experiments with 13C-labeled substrates, the mechanism via carbon shift route was revealed.[5]

Our current research focuses on synthesis of other Sn-OFs upon variation of the linker structure, further insight into structure-performance correlations for catalysis by Sn-OFs, as well as expansion of scopes of rare monosaccharides prepared by epimerization catalyzed by Sn-OFs.

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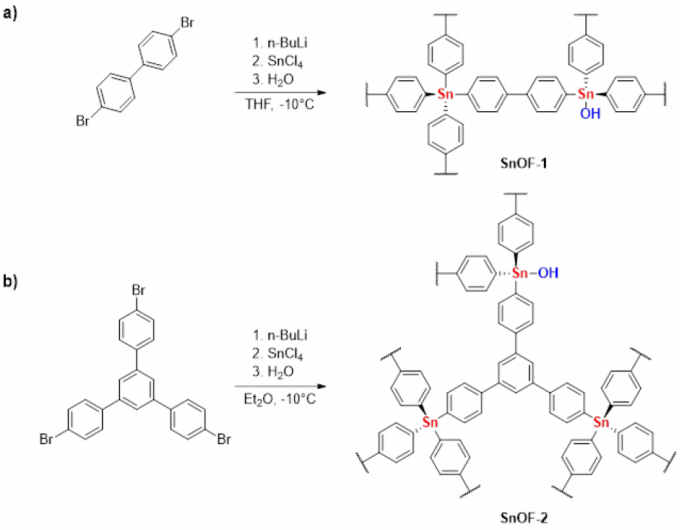
FIGURES



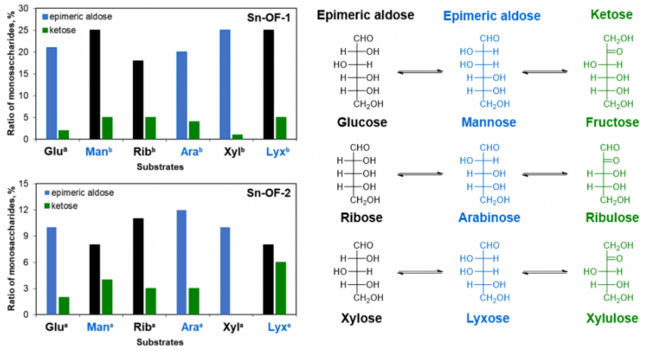


FIGURE 1

Synthesis of poly(arylstannanes) by an organolithium route yields 3D-crosslinked porous tin-organic framework with stannanol groups as catalytically active structural defects.

a) Synthesis of Sn-OF-1

b) Synthesis of Sn-OF-2

FIGURE 2

Results of the catalytic tests (left); Schemes of the tested isomerization- and epimerization equations (right).

a: Reaction conditions: 5 mL of 10 wt.% substrate solution, 100 mg of catalyst, 100°C, 1.5 h, 750 rpm.

b: Reaction conditions: 5 mL of 5 wt.% substrate solution, 100 mg of catalyst, 100°C, 3.0 h, 750 rpm.

KEYWORDS

Porous organic frameworks | Epimerization | Isomerization | Aqueous solution

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