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Xylose Isomerization to Xylulose and its Dehydration to Furfural in Aqueous Media

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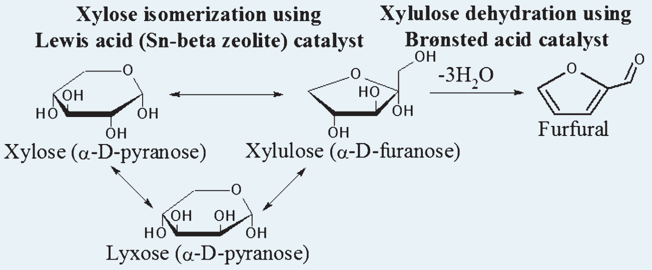
Supporting Information

ABSTRACT: A nonenzymatic route for xylose isomerization in an aqueous medium using zeolite Sn-beta as a catalyst is demonstrated. Xylulose and lyxose are the primary and secondary products. The maximum yield to xylulose is 27%, with an 11% yield to lyxose at ∼60% xylose conversion at 100 °C. When the Sn-beta zeolite is combined with a Brønsted acid catalyst, furfural forms in a single pot from xylose in an aqueous medium at much lower temperatures than typically employed for this reaction.



KEYWORDS: xylose, xylulose, isomerization, Sn-beta, zeolite, furfural

INTRODUCTION

The declining availability of petroleum reserves has generated a strong interest in developing technologies that convert biomass into biofuels and biochemicals.[1−5] The hemicellulose fraction of lignocellulosic biomass, which constitutes ∼25−35% on a dry basis, is rich in pentoses.[2] Xylose is the most prevalent pentose produced via hydrolysis. There has been much interest in converting xylose to ethanol using fermentation[6−8] and to furfural by a catalytic route.[4,9,10]

A challenge to the utilization of pentoses is that *Saccharomyces cerevisiae*, the most common yeast used for ethanol production, does not metabolize xylose.[11] There have been efforts to genetically modify microorganisms to ferment xylose into ethanol. However, a robust industrial process has not yet been developed.[8,11−13] A key step in xylose fermentation involves its isomerization to xylulose, which is subsequently fermented to ethanol.[7]

An alternative approach to utilize xylose entails its thermochemical conversion into furfural, which is a common industrial chemical derived from lignocellulosic biomass with an annual production volume of more than 200,000 tons.[14] The first industrial furfural production process was established by Quaker Oats in 1921. In this process, oat hulls are converted into furfural using concentrated sulfuric acid[15] and high-pressure steam to supply heat and strip out furfural. The direct xylose dehydration into furfural has an activation barrier of ∼30 kcal/mol,[17] and hence, it is carried out at high temperatures (>150 °C) in an aqueous medium.[4] Under these conditions, the furfural yield is ∼30% when carried out in a single-phase system, mainly because of side reactions. The furfural yield can be enhanced using continuous extraction with an organic solvent in a liquid−liquid biphasic system[4,16] or using a carrier gas to strip out the furfural.[15,17] Other processes have been developed,[18] and different acid catalysts have been tested for converting xylose into furfural;[4] however, processes that are more in line with green chemistry principles and of higher furfural selectivity are still needed.[9]

The conversion of xylose to furfural could proceed in two steps by the isomerization of xylose to xylulose, followed by xylulose dehydration to furfural.[19] This was achieved in a one-pot reactor using hydrotalcite as the isomerization catalyst, Amberlyst-15 as a Brønsted acid catalyst, and *N*,*N*-dimethylformamide (DMF) as the solvent to obtain 41% yield of furfural in 3 h at 100 °C. The same reaction pathway was also proposed in *N*,*N*-dimethylacetamide and ionic liquids using chromium halide as a catalyst at moderate temperatures[14] to achieve 55% yield of furfural. Despite the improved yield of furfural at low temperatures, both studies employed high-boiling-point organic solvents, a choice that greatly increases the cost of the separation of furfural from the solvent.

The isomerization of xylose to xylulose followed by dehydration to furfural parallels the conversion of hexoses, for example, the isomerization of glucose to fructose followed by dehydration of fructose to 5-hydroxymethyl furfural (HMF). Moliner et al. have investigated the isomerization of glucose to fructose using the Sn-beta zeolite with yields comparable to biological catalysis.[20,21] Since first synthesized by Corma et al.,[22] this material has successfully been employed as a catalyst in a number of reactions, including the Meerwein−Ponndorf−Verley (MPV) reduction of carbonyl compounds,[23] the production of lactate derivatives from monosaccharides in methanol,[24] and the conversion of trioses to alkyl lactates in the presence of alcohol.[25]

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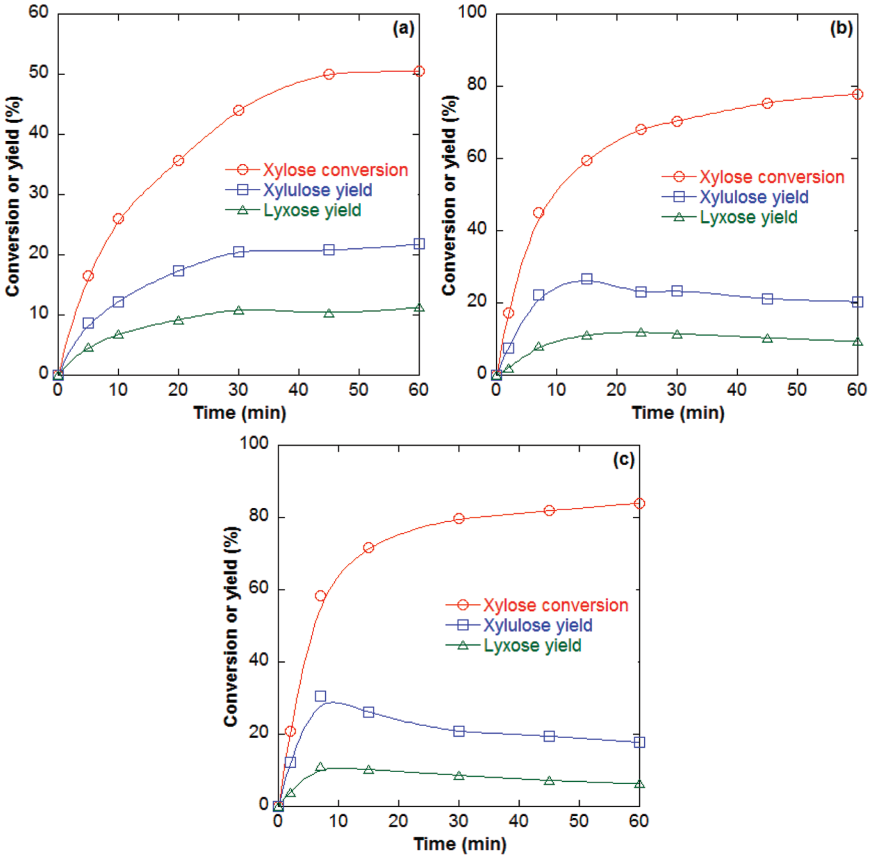


Figure 1. Reaction kinetics of xylose isomerization in an aqueous medium using Sn-beta as a catalyst at (a) 80, (b) 100, and (c) 110 °C. Reaction conditions: initial xylose 10 wt %, xylose to Sn molar ratio of 50:1, reactor volume of 1 mL.

Boronat et al. showed that the active sites in the MPV reaction are partially hydrolyzed Sn−OH groups.[26] Recent NMR studies have showed that the Sn-beta catalyst isomerizes glucose to fructose via 1,2 intrahydride transfer.[27]

Given the potential advantages of heterogeneous catalysts over biological ones,[20] here we investigate the Sn-beta zeolite for the xylose isomerization in aqueous medium and demonstrate that this material can efficiently catalyze this reaction. By combining the Sn-beta with a Brønsted acid catalyst, it is shown that furfural can be prepared in one step from xylose at temperatures below 120 °C in an aqueous medium.

EXPERIMENTAL SECTION

Material Synthesis and Characterization. Sn-containing zeolite beta was synthesized in a fluoride medium following the published protocol[22] (see the Supporting Information). X-ray diffraction patterns of the as-made and calcined samples confirm the structure of the Sn-beta (Figure S1) and are comparable to those of Corma and co-workers.[28] Thermogravimetric analysis of the as-made sample in air showed a total weight loss of ∼19 wt % when heated to a temperature of 800 °C. Assigning the weight loss below 150 °C to water desorption and above this temperature to the decomposition and oxidation of the organic structure director (tetraethylammonium, TEA^+) yields 0.4 wt % of water and 18.7 wt % of organic material. The latter corresponds to 6.8 TEA^+ cations per unit cell, similar to the organic content usually reported for this zeolite when prepared with TEA^+ OH^- as the structure director.[29]

Low water content is generally observed for high-silica zeolites prepared in a fluoride medium and is probably a consequence of the low defect concentration (lack of internal silanol groups) of the material. This procedure leads to micrometer-size zeolite agglomerates composed of smaller crystals (Figure S2). On the basis of N_2 adsorption isotherms, the BET external surface area of the crystals is 100 m^2/g (measured before removal of the structure director), with a micropore volume of 0.16 cm^3/g as determined using the *t*-plot method. ICP−AES analysis showed that the Sn/Si molar ratio of the calcined Sn-beta sample is 0.01, similar to the nominal ratio of the synthesis gels. The UV−visible diffuse reflectance spectrum of the calcined Sn-beta sample (not shown) is similar to spectra previously reported[20] and does not contain any significant absorption bands in the 220−800 nm spectral range.

These results indicate that the Sn-beta samples prepared here have properties similar to those reported elsewhere.[20,28,30−33] When the Sn-beta catalyst was tested in the glucose isomerization reaction, it gave reaction rates comparable to those reported recently[20] (see Table S1).

Catalytic Tests. Figure 1 shows the time evolution of xylose isomerization to xylulose in an aqueous medium using the Sn-beta catalyst at 80, 100, and 110 °C. Xylulose is the main product, but lyxose, another isomer of xylose, is also observed; these reactions are depicted in Scheme 1. The yields of xylulose and lyxose reach a maximum and then decrease with time as a result of side reactions that consume these two products while reaching partial equilibrium with each other. The maximum yield to xylulose was 27%, with a corresponding yield to lyxose of 11%

at a xylose conversion of ~60% in ~7 min at 110 °C and 15 min at 100 °C. The apparent activation energy of consumption (12.5 kcal/mol) was estimated from an Arrhenius plot of the initial rates. Our results parallel those of glucose isomerization to fructose and mannose with yields of 31% and 9%, respectively, at a glucose conversion of ~54% in ~30 min at 110 °C.[20]

The Sn-beta catalyst was regenerated by calcination at 550 °C after the reaction and used to carry out the reaction a total of three times. There was some loss of catalyst during the separation and regeneration process; therefore, the reaction volume was adjusted to maintain identical catalyst concentration at 72 mg/mL. There is no substantial change in the xylose conversion (~5% drop between reactions 1 and 3, as shown in Table 1) or selectivity when compared with the fresh catalyst. These experiments also suggest that there is no significant leaching of Sn during reaction because otherwise, a monotonic decrease in yield would be observed over the series of reaction tests.

Dimethyl sulfoxide (DMSO) is often used as an additive to water to suppress side reactions in homogeneous acid-catalyzed reactions and was employed here as solvent under the same experimental conditions. But DMSO was, in fact, found to inhibit the xylose isomerization reaction (Table S2), possibly because DMSO, a Lewis base, competes with xylose for the Lewis acid sites in Sn-beta. This finding is consistent with a heterogeneous process rather than a homogeneous reaction.

Scheme 1. Schematic Representation of Xylose Isomerization Using the Sn-beta Zeolite and the Xylulose Dehydration Using a Brønsted Acid Catalyst

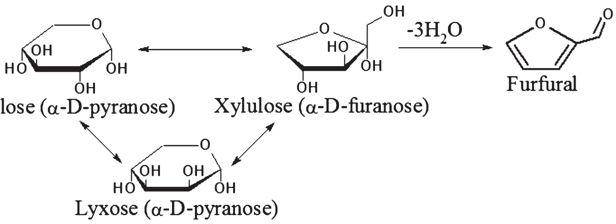


Table 1. Reusability of the Catalyst in the Xylose Isomerization Reaction[a]

	xylose conversion (%)	xylulose yield (%)	lyxose yield (%)
1 fresh catalyst	84.6	18.4	5.3
2 regeneration I	83.2	18.7	5.3
3 regeneration II	79.7	21.3	5.9

[a] Reaction conditions: initial xylose 10 wt %; xylose to Sn molar ratio of 50:1; 110°C.

To assess the possibility of a single pot furfural formation from xylose via xylulose in an aqueous medium, both hydrochloric acid (HCl) and cation exchange resin Amberlyst-15 were examined as Brønsted acid catalyst additives to zeolite Sn-beta (Table 2). Although xylose does not react in Amberlyst-15 or HCl at low temperatures, when xylulose is the reactant, its conversion is ~66%, and the yield to furfural is 24%. This result supports a reaction network in which xylulose dehydrates rapidly to furfural via Brønsted acid catalysis and xylose is isomerized to xylulose with a Lewis acid catalyst. When Sn-beta is combined with Brønsted acid catalysts, xylose is converted into furfural via xylulose in a single pot (Table 2). A high conversion of xylose was obtained, although the yield to furfural was 9.5% with Sn-beta and Amberlyst-15 and 14.3% with Sn-beta and HCl (0.1 M). Overall, these results demonstrate that xylose can be converted to furfural catalytically at much lower temperatures (110 °C) than in previous reports (>150 °C).[4,18] We expect that the yield to furfural can be increased by extraction into an organic phase while the reaction occurs in the aqueous phase, as observed for the glucose-to-HMF reaction.[21]

The presence of other pentoses (namely, arabinose, lyxose, ribose, xylulose and ribulose) was examined, and only xylulose and lyxose were found in the products. Formation of xylulose and lyxose requires either functional group rearrangement or a configuration change around the C1 and C2 carbon atoms, whereas formation of other pentoses would involve changes around at least one other carbon atom. This indicates that the active site of the Sn-beta zeolite interacts with the carbonyl group of C1 and the adjacent hydroxyl group on C2. This mechanism is similar to that reported for Sn-beta-catalyzed MPV reduction of carbonyl compounds.[26] A plausible reaction pathway for xylose isomerization to xylulose and lyxose using the Sn-beta zeolite is presented in Scheme 2. The xylose-to-xylulose reaction path is analogous to the glucose-to-fructose isomerization proposed by Roman-Leskov et al.[27,34] In addition, the proposed mechanism accounts for the observed xylose epimerization to lyxose.

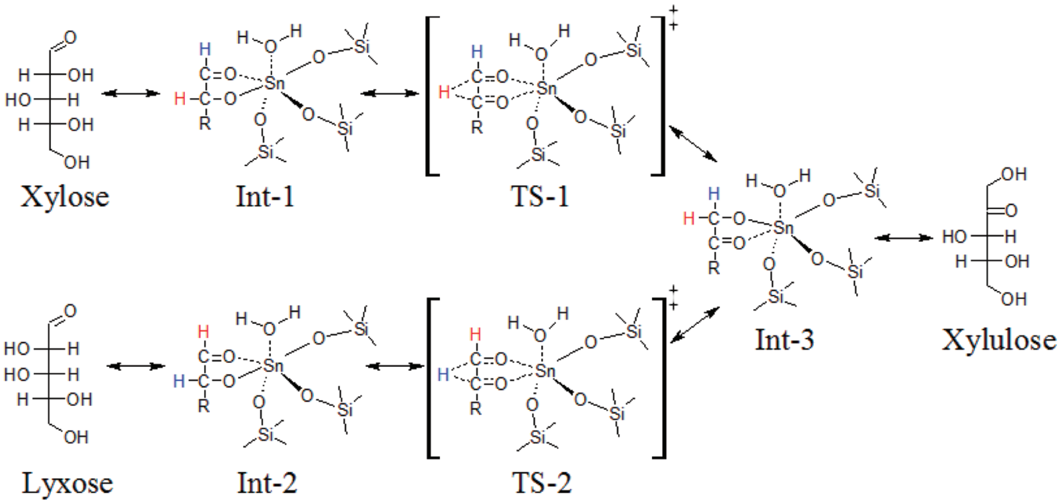
The key intermediate in the mechanism is the one denoted as Int-3. There are three possible reaction channels for this

Table 2. Xylose Reaction in an Aqueous Medium, Using Sn-beta and Possibly a Brønsted Acid Catalyst[b,a]

				yield (%)		
entry	catalyst	time (min)	conversion (%)	xylulose	lyxose	furfural
1[c]	$SnCl_4.5H_2O$	60	6.8			
2	Amberlyst-15	60	0.3			
3[d]	Amberlyst-15	60	65.6			23.5
4	Amberlyst-15 + Sn-beta	60	82.7	18.2	5.1	4.7
5	Amberlyst-15 + Sn-beta	180	92.0	10.2	1.7	9.5
6	HCl (0.1 M)	180	2.1			
7	HCl (0.1 M) + Sn-beta	60	76.7	20.9	7.5	3.8
8	HCl (0.1 M) + Sn-beta	180	83.9	11.2	3.8	14.3

[a] Third entry refers to xylulose reaction[d]. [b] Reaction conditions: xylose 10 wt %, 100 mg Amberlyst-15, xylose-to-Sn molar ratio of 50:1, 110 °C, reactor volume = 1 mL. [c] Homogeneous catalysis using $SnCl_4 \cdot 5H_2O$ to assess the activity of Sn in the homogeneous environment. [d] Xylulose 1.2 wt % was the initial substrate.

Scheme 2. **Plausible Reaction Mechanism for Xylose Isomerization into Xylulose and Lyxose Using Sn-beta As a Catalyst**



metastable state. A proton transfer from the protonated hydroxyl group of Sn to the O1 oxygen of the oxygenate leads to xylulose formation. The other two channels involve hydride transfer from the C1 carbon back to the C2 carbon. Depending on which of the two hydrogens (shown in red and blue) migrates, the reactant (xylose), through the transition TS-1, or the xylose epimer lyxose, through the transition state TS-2, is obtained. This is because one of the two hydrogen atoms lies above the plane formed by the ring structure C1−O1−Sn−O2−C2 and the other lies beneath that plane; either one of them can migrate, resulting in either xylose or lyxose formation.

In summary, it has been shown that Sn-beta is an effective catalyst for the isomerization of xylose into xylulose in an aqueous medium at temperatures as low as <100 °C. This reaction further demonstrates the efficacy of Sn-beta as a catalyst for isomerization of various sugars. The Brønsted-acid-catalyzed dehydration of xylulose to furfural was found to be faster than that of xylose to furfural, and combining Sn-beta with a Brønsted acid catalyst can produce furfural from xylose in an aqueous medium and in a single pot at much lower temperatures than previously reported.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details about the Sn-beta synthesis and characterization and experimental method and additional reaction results are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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