

Production of building blocks for biodegradable polymers from simple sugars using Sn-BEA zeolite

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Introduction

Taarning and coworkers [1] found that Sn-BEA zeolite displays high activity and selectivity for the conversion of mono- and disaccharides to lactic acid derivatives in methanol. Recently, Bell and coworkers [2] identified a significant fraction of hydroxyalkanoic acids and their derivatives when xylose and glucose were reacted in the presence of Sn-BEA in water. α -hydroxy acids comprise are potential monomers for the synthesis of hyper-crosslinked, biodegradable polymers. Dumesic and coworkers [3] found that polar aprotic organic solvents such as γ -valerolactone (GVL) cause significant increases in reaction rates compared to water in addition to increased product selectivity for Brønsted acid-catalyzed reactions like conversion of xylose into furfural, dehydration of 1,2-propanediol to propanal and for the hydrolysis of cellobiose to glucose. Here we report a similar effect for the Lewis acid-catalyzed conversion of C5 and C6 carbohydrates to α -hydroxy acids. We demonstrate that the combination of a Sn-Beta zeolite with mainly Lewis acidity prepared using a post-synthetic procedure and a solution of GVL and water as solvent is an effective catalytic process for the production of α -hydroxy acids from C5 and C6 sugars.

Materials and Methods

The Sn-Beta zeolite was synthesized using the procedure reported by Sels et al. [4]. Commercial Beta zeolite (Grace Davison Division) with a Si/Al ratio of 15 was dealuminated by stirring in 7 or 14 M aqueous nitric acid solutions at 353 K overnight. Afterwards the powder was filtered, rinsed with water and dried. Tin (IV) was grafted on the dealuminated sample by suspending it in isopropanol and adding $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. The solution was refluxed under N_2 for 7 h. The sample was calcined using a ramp of 3 K min^{-1} to 473 K, kept at 423 K for 6 h, ramped to 823 K and kept at 823 K for 6 h. The catalysts were characterized using nitrogen adsorption, X-ray Diffraction, X-ray Photoelectron Spectroscopy, Fourier Transform Infrared Spectroscopy and Inductively Coupled Plasma Atomic Emission Spectroscopy. For reaction kinetics experiments, a solution containing 46 mg of sugar, 3 g of solvent (either water or 9:1 GVL:H₂O), and 33 mg of catalyst were added in 10 mL thick-walled glass reactors with a small magnetic stir bar. The reactors were placed in an oil bath at 433 K and stirred at 700 rpm. Reactors were removed from the oil bath at specific reaction times and cooled by placing in cold water. Concentrations in liquid solution were quantified using a Waters 600 HPLC system with a Waters 2410 refractive index detector and an ion-exclusion column (Bio-Rad Aminex HPX-87H). The mobile phase used was a 0.005 M sulfuric acid solution at a flow rate of 0.6 mL min^{-1} and a column temperature of 353 K.

Results and Discussion

Highly crystalline Sn-Beta zeolite catalysts were synthesized with compositions ranging from 0.28% to 4.12% Sn (Si/Sn = 650 to 40). XPS analysis did not show evidence of surface Al. Some representative experimental results for the conversion of fructose to α -hydroxy acids with Sn-Beta zeolite catalyst are shown in Table 1. The results indicate that when the reaction

is conducted using GVL:H₂O as solvent the turnover frequency (TOF) is 2.6 times higher than in the presence of only water. Furthermore, the yields at high conversion show a significant improvement when the reaction is conducted in GVL:H₂O as shown in entries 2 and 4 with increases of 1.6, 2.0, and 3.0 times for lactic acid, 2,4,5,6-tetrahydroxyhexanoic acid, and 2-hydroxybut-3-enoic acid, respectively. When glucose is used instead of fructose, the results are similar at high conversions, but at low conversions glucose is rapidly isomerized to fructose. For fructose, when 0.23 mM of K₂CO₃ [5] is added to the reaction solution, we observe an additional increase in the reaction rate and the yield towards lactic acid is more than doubled compared to the results without K₂CO₃.

Table 1. Conversion of fructose to lactic acid in different solvents in the presence of Sn-Beta zeolite.^a

Entry	Solvent	Catalyst	Time (h)	Conversion (%)	LA (%)	HHA (%)	HBA (%)	Glu (%)
1	GVL:H ₂ O	Sn-Beta	0.25	65	24	10	8	4
2	GVL:H ₂ O	Sn-Beta	1	92	32	13	6	3
3	H ₂ O	Sn-Beta	1	60	18	5	2	14
4	H ₂ O	Sn-Beta	5	90	20	10	2	31
5	H ₂ O	No cat	1	8	0	0	0	3
6	GVL:H ₂ O	No cat	0.5	6	0	0	0	3

^a Reactions were carried out at 433 K in a batch reactor containing (46 mg) of fructose, (3 g) of solvent and (33 mg) of Sn-Beta where indicated. The ratio GVL:H₂O was 9:1. The yields are designated as: LA is lactic acid, HHA is the sum of 2,4,5,6-tetrahydroxyhexanoic acid and 3-deoxy-D-xylo-hexonic acid γ -lactone, HBA is 2-hydroxybut-3-enoic acid, and Glu is glucose. The yields for levulinic acid and hydroxymethylfurfural are not shown for simplicity.

Significance

The use of Sn-Beta zeolite prepared using a post-synthetic procedure amenable to scale up and GVL:water as solvent offers a viable pathway for the conversion of sugars to α -hydroxy acids with potential for biodegradable polymers in high yields.

References

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