New Heterogeneous Catalysts for Converting Sugars in Aqueous Media

by

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The isomerization of glucose into fructose is a large-scale reaction for the production of high-fructose corn syrup, and recently, is being considered as an intermediate step in the possible route of biomass to fuels and chemicals. Here, it is shown that a large pore zeolite that contains tin (Sn-Beta) is able to isomerize glucose to fructose in aqueous media with high activity and selectivity. Specifically, a 10 wt% glucose solution containing a catalytic amount of Sn-Beta (1:50 Sn:glucose molar ratio) gives product yields of approximately 46% (w/w) glucose, 31% (w/w) fructose, and 9% (w/w) mannose after 30 and 12 minutes of reaction at 383 K and 413 K, respectively. This reactivity is achieved also when a 45 wt% glucose solution is converted. The Sn-Beta catalyst can be used for multiple cycles, and the reaction stops when the solid is removed, clearly indicating that the catalysis is occurring heterogeneously. With isotopically labeled glucose, it is demonstrated (^{1}H and ^{13}C MAS NMR spectroscopy) that the isomerization reaction catalyzed by Sn-Beta in water proceeds by way of an intramolecular hydride shift, confirming that framework tin centers in Sn-Beta act as Lewis acids in aqueous media. Most importantly, the Sn-Beta catalyst is able to perform the isomerization reaction in highly acidic, aqueous environments with equivalent activity and product distribution as in media without added acid. This enables Sn-Beta to couple isomerizations with other acid-catalyzed reactions, including hydrolysis/isomerization or isomerization/dehydration reaction sequences, including starch to fructose and glucose to 5-hydroxymethylfurfural (HMF).