Sorbitol Conversion Over Solid Acid Catalysts

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Introduction
Anhydro sugar alcohols, such as isosorbide, are known for their uses in therapeutics, food additives, surfactants and more recently in PET polymers. Isosorbide is a derivative of sorbitol which can be derived from various renewable resources. It is well known that isosorbide is produced through dehydration of sorbitol using dehydration catalysts, typically strong acids. Examples of acid catalysts used commercially include mineral acids such as H₂SO₄, HCl and H₃PO₄. The dehydration reaction is operated in a homogeneous mode. Due to the corrosive properties of mineral acids and the nature of homogeneous operation, process scale-up and environmental concerns are major challenges. The intention of our current research is to explore possibilities of replacing mineral acids with environment benign solid acid catalysts in sorbitol conversion processes. Activities of various solid acid catalysts, including zeolites, resins, clays, sulfated zirconium superacids and supported heteropoly acids are compared against sulfuric acid. In this paper, discussion will be focused on two catalyst systems, supported heteropoly acid (supported HPA) and zeolite catalysts. The acidity, pore structure and HPA dispersive state as well as the crystal structure of support have been investigated by XRD, IR and TPD. The activity, selectivity and stability of the supported HPA catalysts could be correlated with the surface acidity/acid strength, the structure of supports as well as time on stream performance. The influence of the support properties on the amount of encapsulation of the heteropoly acid molecule has been investigated to clarify the key factors that determine activity in aqueous solutions. Particular properties under investigation are the Cs concentration for SiO₂ supported HPA, Si/Al ratio for zeolite catalysts and zeolite supported-HPA.

Results and Discussion
We have previously reported on immobilization of HPA on SiO₂ support using highly dispersed Cs salts as anchors.(2,3) Silica support is impregnated in Cs₂CO₃ aqueous solution, dried at 110°C in vacuum overnight and calcined at 500°C for 2 hours. The resultant solids are immersed in phosphotungstic acid solution in butanol, dried at 110°C in vacuum overnight and calcined at 300°C for 2 hours. The ratio of Cs⁺ to proton is designed to form Cs₂.₅H₀.₅PW₁₂O₄₀ salts on the support while the amounts of Cs₂.₅H₀.₅PW₁₂O₄₀ salts on the catalyst are changed from 26 to 82 wt%. The testing of catalytic performance is conducted in a batch reactor under conditions of 135°C and 70 mm Hg vacuum. Figure 1 illustrates the effect of Cs₂.₅H₀.₅PW₁₂O₄₀ loading on sorbitol conversion. The volcano shaped cure indicates that an optimal conversion can be reached at Cs₂.₅H₀.₅PW₁₂O₄₀ loading of about 60%. The loss of activity at
Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ concentration higher than 60% cannot be related to the loss of surface area. Interestingly, theoretical calculations reveal that a 60% Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ loading corresponds to mono layer coverage of HPA on SiO$_2$. This may explain why conversion of sorbitol declines sharply at Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ concentrations higher than 60%. Ideally, monolayer Cs is required to form strong bonding between SiO$_2$, Cs and HPA. When excess Cs is doped, the excess HPA may not interact with Cs cations, leading to HPA leaching during the reaction. Product characterization coupled with kinetic data elucidate the reaction pathway involved in sorbitol conversion. Through fundamental understanding of reaction mechanism, we are able to enhance catalyst activity while still maintain high selectivity to desired products.

References