Hydrogen Production from Aqueous Phase Reforming of Sorbitol and Related Oxygenated Hydrocarbons

James Cao[1,2], Gordon Xia[1], Alex Platon[1,3], David King[1], Yong Wang[1*]
[1] Pacific Northwest National Laboratory, PO Box 999, K8-93, Richland, WA99352
[2] ExxonMobil Chemical Company, 4500 Bayway Drive, Baytown, TX 77520
[3] ConocoPhillips Company, 1000 S Pine, 4663 RW, Ponca City, OK 74602
* Yong.Wang@pnl.gov

Introduction

Catalytic conversion of biomass-derived feedstocks, such as ethanol, sugars, sugar alcohols, polyols, and less refined hemicellulose or cellulose, may provide a means for hydrogen production through a renewable source. Because of the relatively high cost of current technologies for utilizing biomass feedstocks compared to fossil fuels, however, biomass to hydrogen conversion processes must be highly efficient in terms of high hydrogen productivity and selectivity. The aqueous phase reforming (APR) of biomass-derived hydrocarbons for hydrogen production that was originally proposed by Dumesic's group appears to be a very promising approach [1,2].

It has been suggested that the kinetic control of reaction pathways in the course of APR processes is essential for good hydrogen productivity. There may be two main reaction pathways involved in hydrogen production: the C-C bond cleavage pathway and the C-O bond cleavage pathway [3]. The former pathway is desired for hydrogen production. The later pathway is more favorable for the formation of alkanes. A good catalyst for hydrogen production should have good C-C bond cleavage and water gas shift activity while keep low C-O bond cleavage activity. In addition, additional reaction pathways can also be controlled by the intrinsic chemical structure of the reactant molecule. To gain more valuable information on the role of chemical structure of the starting material (for example carbon number and proximity of C-OH groups) on the reaction rate and hydrogen selectivity, we have focused on the fate and relative reactivity of sorbitol and several oxygenate intermediates or byproducts that can be formed during low-temperature aqueous reforming of sorbitol. These oxygenate intermediates include propylene glycol (PG), glycerol (Gly), ethylene glycol (EG), 1-propanol (1-PrOH), ethanol (EtOH), and 1,3 -propanediol (1,3-PPD), which were studied under the conditions similar to sorbitol reforming.

Materials and Methods

A typical catalyst of 3wt% Pt/Al_2O_3 was prepared by incipient wetness method using an active neutral γ-Al_2O_3 support impregnated with a $Pt(NH_3)_4(NO_3)_2$ aqueous solution. The as-synthesized sample was dried at 105ºC in a vacuum oven and calcined at 280ºC in air. The catalyst was loaded in a stainless steel fixed bed reactor and reduced in 20sccm H_2 at 260ºC for 2 hrs. The system was purged and pressurized with N_2 for a desired pressure. For a typical run, the system temperature was raised to 225ºC at 420psi before pumping a preheated 10wt.% aqueous solution of oxygenated hydrocarbon substrate into the reactor system.. The gas effluent was analyzed using a GC and the liquid effluent was analyzed using a HPLC.

Results and Discussion

As shown in Figure 1, the conversion and selectivity toward hydrogen were different for each of these species. Specifically, the reaction rates of PG, 1,3-PPD, and GLY were all faster than that of the parent sorbitol molecule. It was also observed that hydrogen productivity from PG, Gly, and EG was more than a factor of 2 higher than the parent sorbitol. On the other hand, EtOH, 1-PrOH, and 1,3 PPD exhibited higher selectivity to alkanes than did sorbitol, while EG showed very low selectivity to alkanes. These results clearly demonstrate that the chemical structures played a critical role in the catalytic reforming processes. The reaction mechanisms involved in these reforming processes may be quite complicated and affected by the nature of catalyst, reaction conditions, and the composition of feed. Further understanding of the relative reactivity of intermediate species as described above may provide the guidance to improve higher hydrogen productivity. For example, some shorter chain polyols such as propylene glycol, glycerol, and ethylene glycol may be preferred to form via pre-hydrogenolysis of sorbitol. New catalyst compositions that can effectively convert these preferred intermediates need to be developed.
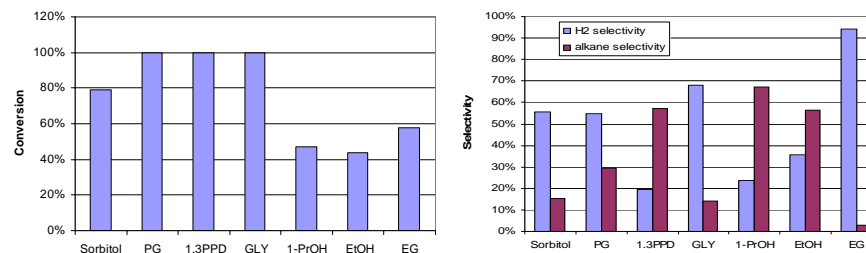

Figure 1: Reactivity of sorbitol and other oxygenated hydrocarbons over 3% Pt/Al_2O_3 catalyst at 225ºC, LHSV of 1.9 h^{-1}, and 420psi system pressure.

Significance

Hydrogen production from aqueous phase reforming of biomass feedstocks still faces major challenges of relatively low reaction rate and poor selectivity to hydrogen. Selectively breakdown of raw biomass feedstocks to shorter chain polyols before the reforming step may facilitate high hydrogen production rates and eventually reduce the cost of the biomass based hydrogen.

References

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