

## Polyol Hydrogenolysis by *in-situ* Generated Hydrogen

Debdut Roy, Bala Subramaniam and Raghunath V. Chaudhari\*

Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66047

\* [rvc1948@ku.edu](mailto:rvc1948@ku.edu)

### Introduction

The demands for technology have always been driven by anticipated changes in the global situation of resources and environmental and societal needs with improved economics. Indeed the gasoline shortages in 70s and the increasing fuel prices have alerted researchers to look for alternative resources and conversion technologies for fuels and chemicals well ahead of time. In this context, renewable bio-resources have been considered as alternatives in different forums and debated on pros and cons for converting these to fuels and chemicals and concluded that “biomass is the only practical source of renewable liquid fuels” [1].

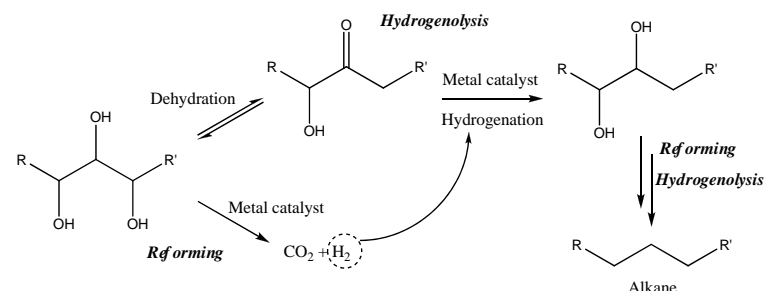
Cellulosic biomass and vegetable oils are considered as important renewable resources for converting to chemicals and fuels. While, the conversion of vegetable oils to bio-diesel has already been at advanced stage of commercialization, the long range sustainability of this resource and the technologies would largely depend on the competitive costs of the end product bio-diesel. Here, the large volume of glycerol produced as a co-product along with bio-diesel has particular significance, the utilization of which is most essential for the overall viability of the approach. Similarly, the sugars derived from the abundantly available biomass converted to polyhydroxy compounds by partial deoxygenation and even to alkanes by complete deoxygenation has huge importance. Recently Dumesic and coworkers [2] have demonstrated that glycerol and sugar alcohols having a general formula of  $C_nH_{2(n+2)}O_n$  are very good candidates for hydrogen production also by aqueous phase reforming (APR). In this presentation, our experimental results on APR and hydrogenolysis of polyol in combination will be discussed, where the hydrogen produced by APR is used for the hydrogenolysis reaction. There are very few reports in the literature on utilization of *in-situ* generated hydrogen for chemical transformations [3]. These reports deal with proving the concept of APR and hydrogenolysis combo reaction and there is huge scope for systematic studies on catalysis and reaction engineering issues to improve the product selectivity. Results on bifunctional catalysts for simultaneous APR and hydrogenolysis reactions, role of supports (especially acidic supports), promoters and metal dispersion characteristics will be addressed in this presentation with glycerol and sorbitol as the model substrates.

### Materials and Methods

The mono-metallic and bi-metallic catalysts on different supports were synthesized by the incipient wetness as well as precipitation methods [4]. Several neutral and acidic supports were selected to study the effect of support acidity especially on the dehydration step involved in the hydrogenolysis reaction as shown in Figure 1. Reactions were carried out with (i) only one metal to see its activity for both the reactions, (ii) physical mixtures of two monometallic catalysts (one for APR and one for hydrogenolysis), and (iii) bi-metallic catalysts to study the effect of their metal-metal interactions.

The APR-hydrogenolysis one pot combo experiments were carried out in a 100 ml Parr autoclave using 10 wt% polyol in water at a range of 473 to 523 K with and without

external hydrogen feed. The liquid phase samples were analyzed using HPLC. The gas phase samples were analyzed at the end of the reaction using GC.



**Figure 1.** Reaction pathway for APR-hydrogenolysis combo reaction of polyols

### Results and Discussion

We report herewith some preliminary results with high conversion and selectivity to deoxygenated polyols for the APR-hydrogenolysis combo reaction with glycerol and sorbitol as substrates. In a typical reaction, >95% conversion of glycerol with 30-40% selectivity of 1,2-propanediol (1,2-PDO) based on initial glycerol charge was achieved with a Pt-Ru catalytic system without using hydrogen. More interestingly, there was no quantitative amount of hydrogen observed in the gas phase sample. This indicates that the hydrogen produced in the reforming step has been utilized *in-situ* in the hydrogenolysis reaction.

### Significance

Generation of *in-situ* hydrogen from renewable resources for chemical transformation has very high impact from energy and environmental point of view. Hydrogen is currently produced from nonrenewable natural gas and petroleum [5]. In the APR process, it can be produced from renewable biomass, and can be utilized completely to produce valuable chemicals and fuels.

### References

1. Bull, T.E. *Science* 285, 1209 (1999)
2. Cortright, R.D., Davda, R.R., and Dumesic, J.A. *Nature* 418, 964 (2002)
3. (a) Huber, G.W., and Dumesic, J.A. *Catalysis Today*, 111, 119 (2006), (b) Randy, D. *WO 2008/069830* (2008)
4. (a) Rajashekharan, M.V. and Chaudhari, R.V. *Cat. Lett.* 41, 171 (1996) (b) Roy, D. and Chaudhari, R.V. *Ind. Eng. Chem. Res.* 44, 9586 (2005)
5. Jacobsen, H. *Angew. Chem. Int. Ed.* 43, 1912 (2004)