Higher Alcohols and Cyclic Acetals from Glycerol

Aiguo Liu*, Chris Luckett, Faye Li, Todd Cole, Wayne Turbeville

Sud-Chemie Inc, 1600 Hill St, Louisville, KY, 40210, USA

** Corresponding author: Fax (502) 634 7265, E-mail: Aiguo.liu@sud-chemie.com*

Introduction

Conversion of simple molecules such as sugar or glycerol that are directly derived from renewable resources into high-valued chemicals or fuels has been the focus of many recent researches [1, 2]. Through in-situ generation of aldols, condensation and acetalization are possible alternative pathways to produce higher alcohols and cyclic acetals for fine chemicals and oxygenated fuel additives [3]. This paper presents preliminary results from a study that used glycerol as a model molecule to probe effects of catalysts and reaction conditions on the distribution of major products and possible reaction pathways.

Experimental

Tests were conducted in an autoclave with a back pressure regulator for constant pressure control. Water, methanol, and ethanol were selected as reaction media and pre-mixed with glycerol. Cu modified ZSM-5 was prepared by dipping the zeolite in $Cu(NO_3)_2$ solution. H-ZSM-5 zeolite, Cu/Cr catalysts are commercial products without further treatment. Reaction products were analyzed by using GC/MS with a carbowax column. Effects of catalysts and reaction conditions on product distribution were measured by the ratios between peak areas of a major compound and 1-hydroxy-2-propanone. Results were normalized to 1-hydroxyl-2-propanone.

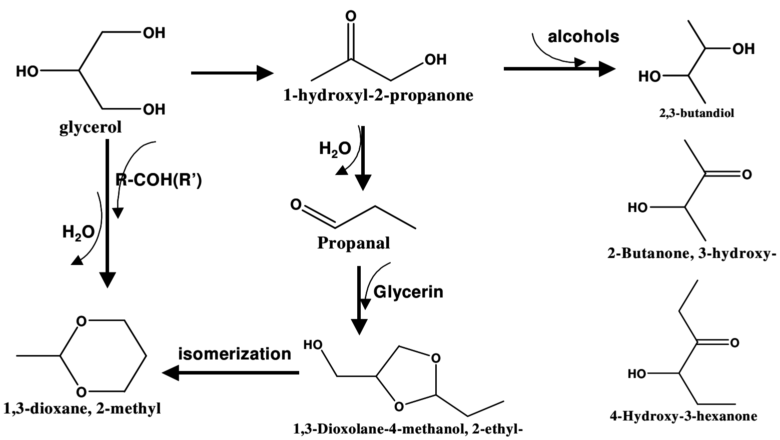

Figure 1. Simplified Scheme of Possible Reaction Pathways

Results and discussion

1-hydroxyl-2-propanone is believed to be the initial dehydration product from glycerin [2]. It can further dehydrate to the formation of alcohol and aldol compounds that lead to reactions of condensation and acetalization. **Figure 1** demonstrates a simplified diagram to show possible major reaction pathways.

Table 1 presented a summary of test results under various catalysts and reaction conditions. Compounds that were most likely derived from glycerin were selected as representative compounds. Results show that higher alcohols (> C4) and various cyclic acetals mainly the 1,3-dioxolane and its derivatives (not shown) were formed. The intra-molecular dehydration of glycerol is assumed to be an initial step leading to an aldol-condensation chain growth with alcohols that are either produced in situ or added as solvent (e.g., methanol) [4]. ZSM-5 zeolite was found essential for the formation of cyclic acetals, which may attribute to the shape selectivity of zeolites. Reductive atmosphere did not significantly alternate the product distribution and water seems inhibitive to the further dehydration of 1-hydroxyl-2-propanone.

Table 1. Relative Concentration of Major Compounds Derived from Glycerol [a]

Cat/Sol/Gas [b]	acetone	propanal	propanol	1-methoxy 2-propanone	3-hydroxy-2-butanol	2-ethyl-4-methanol-1,3-dioxolane-
Cu-Z/M/H_2	0.043	0.146	0.480	0.433	0.110	0.488
Cu-Z/M/N_2	0.010	0.104	0.033	1.342	0.338	0.058
Cu/M	0.114	- [c]	0.145	0.067	0.228	-
Z/H_2O/N_2	-	-	-	-	-	0.467
Z/EtOH/N_2	0.563	12.31	7.813	-	-	0.750

Note: a. Ratio of peak area normalized to 1-hydroxyl-2-propanone; b.Catalysts: Cu – copper chromite, Cu-Z – Cu dipped on ZSM-5; Media: M – methanol, EtOH – ethanol; atmosphere: controlled by H_2 or N_2 at 68 Bar constant pressure. c. "-" not detected by GC/MS

Conclusions

Results indicate that it is possible to convert glycerin to other fine chemicals beyond the PG. However, complexity of reactions requires more selective catalysts and more detailed investigation of reaction conditions so that a better selectivity for targeted products can be achieved.

References

1. Huber, G.W., Chheda, J.N., Barrett, C.J., and Dumesic, J.A., *Science,* 308 (2005), 1446
2. Dasari, M.A., Kiatsimkul, P., Sutterlin, W.R., and Suppes, G.J., *Appl Catal A.,* 281 (2005), 225
3. Deutsch, J., Martin, A., and Lieske, H., *J. Cat*., 245 (2007), 428
4. Xu, M. and Iglesia, E., *J. Cat.,* 188 (1999), 125