

Aqueous Phase Reforming of Glycerol: Reaction Pathways, Base Effects, and Catalyst Deactivation

D.L. King^{*1}, Y. Wang¹, G. Xia¹, Y. Yang¹, D Heldebrant¹, L. Zhang¹, and T. Peterson²

¹Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 (USA)

²Dow Chemical Company, 2030 Dow Center, Midland MI 48674

[*david.king@pnl.gov](mailto:david.king@pnl.gov)

Introduction

Reforming of sugar alcohols and polyols at elevated pressures and moderate temperatures (<275°C) in aqueous phase (APR) is a promising approach for the thermochemical production of hydrogen from renewable biomass feedstocks¹. Avoidance of undesired gas phase hydrocarbons and minimization of byproduct aqueous-phase oxygenates requires kinetic control of reaction pathways by careful choice of catalyst and conditions. Although much progress is being made in developing and commercializing APR technology, an understanding of the reaction pathways available to these compounds is just now emerging, mostly in the context of converting sugars and sugar alcohols to more conventional transportation fuels².

The APR studies to be described here have focused primarily on understanding the aqueous phase chemistry of glycerol conversion, using carbon-supported Pt and Pt-Re catalysts. The reaction pathways available to glycerol are similarly available to sugar alcohols such as sorbitol, and glycerol provides a more tractable aqueous phase product set to more clearly delineate these pathways. To facilitate identification of reaction intermediates, as well as to obtain a quantification of activity in terms of turnover frequencies, reactions were carried out at relatively high space velocities. We studied the system at neutral pH as well as with intentionally added base to determine the latter's potential to reduce hydrocarbon formation.

Materials and Methods

Catalysts were prepared by incipient wetness impregnation using $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and perrenic acid (HReO_4) on coconut carbon (surface area 550 m^2/g). Pt loading was held at 3wt.% and Re loadings varied from 0 to 3.16wt.%. About 200mg of catalyst was loaded into a small microchannel fixed bed reactor and reduced in flowing H_2 at 280°C. Following reduction, the catalyst was cooled to reaction temperature and an aqueous mixture of glycerol (10 wt.%) flowed over the catalyst using a HPLC pump. Operating temperature was typically 225-230°C and operating pressure 30 bar, with a WHSV (glycerol) of 5.6 h^{-1} . Product determination utilized two separate analyses, one for gas phase products (Agilent micro GC) and a second for liquid products (HPLC), calibrated using pure compounds. Mass balanced was typically 90+%. For some of the experiments, 1 wt.% KOH base was added, although use of alternate bases was also investigated. Fresh and spent catalysts were characterized for total surfaced area (BET), and metal surface area (CO chemisorption).

Results and Discussion

APR of glycerol over Pt/C and Pt-Re/C catalysts without and with 1%KOH base addition added to the feed is shown in Figure 1. Addition of Re addition to Pt increases the glycerol conversion significantly, at the expense of a somewhat higher selectivity toward gas phase hydrocarbons relative to hydrogen. In the liquid phase, the 3%Pt/C catalyst produces primarily

propylene and ethylene glycol, whereas with the addition of Re the glycols decrease somewhat but there is a significant production of monohydric alcohols and carboxylic acids. We postulated that the production of alcohols as well as light alkanes could be attributed to sequences of dehydration followed by hydrogenation, which might be facilitated by the presence of Re in the catalyst. 1% KOH was added to the solution in an effort to retard the dehydration pathways. This resulted in a dramatic initial increase in H_2 gas phase selectivity, as the light hydrocarbon products were drastically diminished, shown in Figure 1b. Correspondingly, there was a greater fraction of carbon products in the liquid phase with the Pt-Re/C catalysts. As the reaction proceeded in the presence of base, there was a decrease in pH, a decrease in H_2 yield, and a decline in overall catalyst activity.

The product selectivity with these catalysts, especially in the presence of base, will be shown to be the result of a combination of heterogeneous and homogeneous reactions. In a simplified scheme, the favored hydrogen production pathway with glycerol is initiated by dehydrogenation to form the corresponding glyceraldehyde, followed by C-C bond cleavage to generate CO and an additional mole of hydrogen via water gas shift. Successive conversions of this type lead to H_2 and CO_2 products. Alternatively, sequences of dehydration followed by hydrogenation can lead to propylene glycol or monohydric alcohols. In the presence of base, initial dehydrogenation appears to be facilitated, but subsequent carbon-carbon bond cleavage appears to be slower, so that the base-catalyzed Cannizzaro reaction and aldol condensation involving glyceraldehyde are facilitated. Generation of carboxylic acids via the Cannizzaro reaction can explain the drop in pH, and formation of various organic polymers via aldol condensation may contribute to catalyst deactivation via catalyst pore plugging and metal surface coverage. We will describe catalyst modifications and experiments with alternate bases aimed at minimizing the base-catalyzed reactions and extending catalyst life.

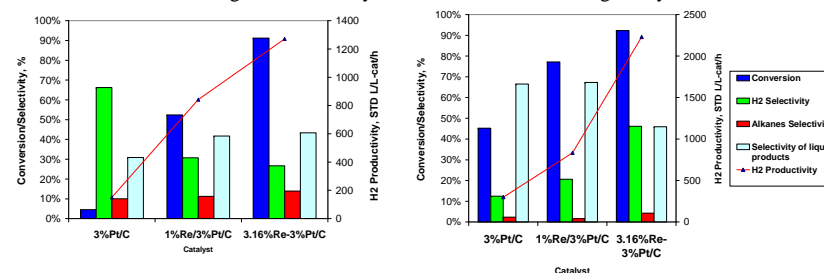


Figure 1. Effects of addition of Re to Pt/C catalyst and the addition of base for glycerol APR, (left) 10wt.% glycerol with out base; (right) 10 wt.% glycerol with 1wt.% KOH.

Significance

Our results point to the importance of understanding the reaction pathways, both heterogeneous and well as homogeneous, in determining product selectivity and yield for APR of glycerol and related sugar alcohols.

References

1. D.A. Simonetti, E.L. Kunkes, and J.A. Dumesic. *J. Catalysis* 247, 298 (2007)
2. J. N. Chheda and J.A. Dumesic. *Catalysis Today* 123, 59 (2007)