

New Catalysts for the Hydrogenolysis of Glycerol and Sugar Alcohols

Johnathan E. Holladay,* James F. White, John G. Frye, Alan Zacher, and Todd Werpy
Pacific Northwest National Laboratory, Richland, WA 99337 (USA)
*john.holladay@pnl.gov

Introduction

Recent interest in production of biodiesel provides an opportunity for developing new products from glycerol. Domestic biodiesel production is expected to grow to 1 - 2 billion gallons by 2010. One billion gallons would result in the production of 770 million pounds of glycerol. The US glycerol market is only 320 million pounds.

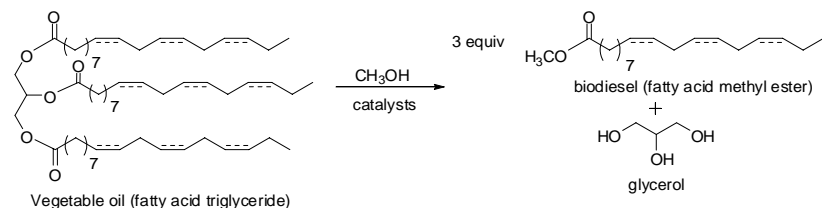


Figure 1. Biodiesel production

Development of value-added products from glycerol can help the total economics of an oilseed biorefinery. Propylene glycol is one such product. This paper will focus on the development of catalysts that can convert glycerol to propylene glycol in high yields. Our work has focused on a class of catalysts based on Re, which as a co-metal imparts important character to the catalysts.¹ The reaction is shown in Figure 2.

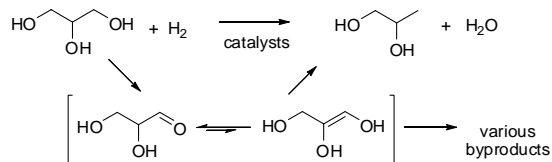


Figure 2. Dehydrogenation of glycerol

Materials and Methods

Catalysts were prepared on various supports. One example was a Calgon 120% CTC coconut carbon. The impregnation volume of metal solution was calculated using the measured incipient wetness of the support; 0.85 cc liquid per gram of carbon for the Calgon support. Nickel was added as a nickel nitrate solution, rhenium was added as perrhenic acid, ruthenium was added as ruthenium nitrosyl nitrate and other metals were added as various salts. Impregnation solutions were added dropwise and the carbon shaken thoroughly at about each

10% addition interval. After the metal addition, the vessel was capped for 15 minutes after which the catalyst was dried at 80 °C under 510 mmHg vacuum.

In batch experiments catalyst, normally 2.5 g, was added into a 300 ml Parr autoclave. The reactor was purged with nitrogen and then reduced under hydrogen atmosphere at elevated temperature. The reactor was then cooled and to room temperature and an aqueous solution of glycerol and sodium hydroxide was added. The reactor was pressurized to a desired pressure with hydrogen and heated to the desired temperature. Samples were pushed out intermittently through a valve dip tube.

In continuous flow experiments catalyst, normally about 30 cc, was packed into a downflow trickle-bed reactor. Hydrogen was passed slowly over the catalyst at atmospheric pressure and the temperature was slowly raised to the desired reduction temperature. The reactor was cooled and flow of an aqueous feed of glycerol and sodium hydroxide initiated. A large set of reaction conditions was tested.

Results and Discussion

Choice of support has a tremendous impact on catalysis performance and stability. We have shown granular and extruded carbon supports to be particularly stable to hydrothermal conditions as measured by crush strength versus silica or alumina supports. Rutile Titanium has also shown high strength. Granular carbons have a very different pore

structure than carbon extrudates which can impact catalyst performance. Finally the support plays a role on selective adsorption of reagents and products, which will be discussed. In addition to the support, the interactions between nickel and rhenium play a pivotal role in the catalyst. An extreme example of the reactivity difference is shown in figure 3 (batch conditions, 200 °C, 1200 psig H₂). In addition to nickel and rhenium we will also discuss results with silver, copper, and ruthenium.

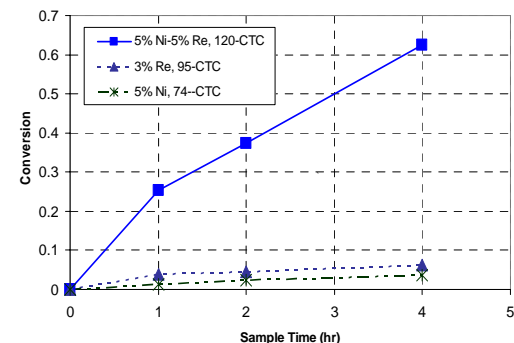


Figure 3. Ni/Re versus Ni and Re catalysts

Significance

Advances in catalysis are important endeavors to empower biorefineries and the use of renewable feeds. This paper presents the development of effective catalysts for aqueous phase processing of sugar alcohols, like glycerol, to propylene glycol and other glycols. Rhenium-containing multimetallic catalysts result in superior conversion and selectivity.

References

1. Werpy; T.A., Frye, Jr., J.G., Zacher; A.H. and Miller; D.J. *US Patent* 6,841,085 (2005).