

Atmospheric Pressure Glycerol Hydrogenolysis over Pt/C, Pt/Al₂O₃, and Copper Chromite Catalysts

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Introduction

Glycerol is a byproduct of biodiesel production via transesterification of triglycerides with methanol (or ethanol). Recently, crude glycerol supply has outstripped demand, and glycerol prices have declined to less than \$0.05/lb. Catalytic technology to produce useful synthetic chemicals from this abundant and renewable resource would provide a potential market for excess glycerol greatly improving the economics of biodiesel production. Propylene glycol (1,2-propanediol, 1,2-PDO) (formally resulting from C-O bond hydrogenolysis) is an attractive target molecule due to an established market and the cost of production via conventional synthetic routes. Methanol (resulting from C-C bond hydrogenolysis) is also attractive since it can be used in biodiesel production. This study specifically focuses on vapor phase glycerol hydrogenolysis at low pressures in an effort to identify catalytic processes that might be easily accessible to biodiesel producers.

Others have investigated glycerol dehydration to acetol in the liquid phase using a copper chromite catalyst [1,2]. More recently, Suppes and coworkers have published results for vapor-phase glycerol hydrogenolysis to 1,2-PDO over copper chromite at near atmospheric pressure. [3,4]. However, most of the published work has employed integral packed bed reactors with product collection and off-line analysis. In this work, we investigated the vapor-phase hydrogenolysis of glycerol over 5 wt.% Pt/C, 5 wt.% Pt/Al₂O₃, and copper chromite catalysts using a microflow reactor with on-line gas chromatography.

Materials and Methods

Carbon- and alumina-supported Pt and copper chromite catalysts were purchased from Alfa Aesar. Catalysts were used as powders after pretreatment in flowing H₂ at 300°C for 1 h. Glycerol (99.5%) was purchased from Fisher Scientific, and ultra-high purity hydrogen and helium (99.999%) were provided by National Welders.

Experiments were performed in a stainless steel vertical down-flow reactor mounted in a tube furnace at atmospheric pressure. The reactor was packed with 0.5 to 1.0 g of catalyst between plugs of quartz wool. A thermocouple inserted in the catalyst bed was used to monitor catalyst temperature. Gas flow rates were controlled by Unit mass flow controllers. The gas composition during reaction was either He, H₂ or 10% H₂ (balance He). A syringe pump was used to inject glycerol into a preheated gas stream to prepare the desired feed concentration (1–8 mol %). The reactor effluent was coupled via a Valco 6-port valve to a gas chromatograph (Perkin Elmer) equipped with an EC-1 capillary column (Grace Alltech) and flame ionization detector (FID).

Results and Discussion

The three catalysts were examined for the vapor-phase hydrogenolysis of glycerol at atmospheric pressure. Some important differences are apparent in the steady-state product distributions obtained using a 2 mol % glycerol feed at 230°C. Over a 5 wt.% Pt/Al₂O₃ catalyst under He, the most abundant products are acetol and acrolein resulting from glycerol dehydration, and introducing H₂ alters the product distribution very little. Acetol and acrolein

are also the majority products over a 5 wt.% Pt/C catalyst under He; however, the catalytic activity is significantly higher. The Pt/C catalyst is also more sensitive to the presence of H₂ than Pt/Al₂O₃. For the Pt/C catalyst, the selectivity towards acetol production increases significantly under 10% H₂. The observed conversion is also significantly higher under H₂ than under He possibly due to inhibition of coking and/or other deactivation processes. At higher temperatures, 275–300°C, the glycerol conversion approaches 100% and the catalyst becomes much more selective for C-C bond hydrogenolysis products formaldehyde and methanol.

Using a copper chromite catalyst, the most abundant reaction product is the double dehydration product acrolein at 240°C under He. Under 1 atm H₂, the most abundant product is acetol, and the yield of acrolein decreases. In addition, the overall conversion increases from 14 to 38%. Using a 1% glycerol feed and 1 atm H₂, the glycerol conversion is approximately 65% and 1,2-PDO is initially the most abundant product, but its concentration decreases with time on stream. Acetol production increases as 1,2-PDO production decreases supporting the hypothesis that 1,2-PDO is produced by hydrogenation of acetol over copper chromite. Initially, 1,2-PDO is also produced under inert conditions over a freshly reduced copper chromite catalyst. However, 1,2-PDO production ceases quickly evidencing that active hydrogen on the catalyst surface is necessary for 1,2-PDO production.

The observed glycerol reaction products can be explained in terms of the network shown in Figure 1. Glycerol can be either singly or doubly dehydrated to give acetol and acrolein, respectively. Subsequent hydrogenation of acetol yields the C-O bond hydrogenolysis product 1,2-PDO over copper chromite. C-C bond hydrogenolysis at higher temperatures over supported Pt yields formaldehyde, methanol and methane.

Significance

Glycerol production is at an all time high due to increased biodiesel production. Catalytic technology to produce value-added chemicals from this abundant bio-renewable compound is of great interest as it lessens our reliance on non-renewable resources.

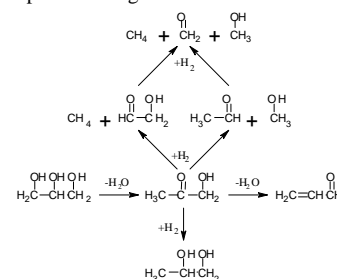


Figure 1. Reaction network showing the relationship between glycerol dehydration and hydrogenolysis products. Glycerol is singly dehydrated to yield acetol which may undergo either an additional dehydration step or hydrogenolysis. Dehydration of acetol yields acrolein, C-O bond hydrogenolysis produces 1,2-propanediol, and C-C bond hydrogenolysis eventually yields methane, formaldehyde, and methanol.

References

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