

Conversion of Sorbitol and Glycerol over Supported Transition Metal Catalysts

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Introduction

The production of biobased organic chemicals has been identified by the National Research Council as the most promising platform for the utilization of renewable biomass as an alternative to petroleum [1]. Cellulosic biomass, like carbohydrates, is considered to be the most abundant organic material on earth [2], and is therefore an ideal feedstock for the production of biobased chemicals. In some processing schemes, conversion of carbohydrates can involve the initial hydrogenation of a simple sugar, such as glucose, to the sugar alcohol sorbitol. The subsequent catalytic hydrogenolysis of sorbitol yields lower molecular weight polyols such as glycerol, ethylene glycol and propylene glycol. Glycerol, which is also a byproduct from biodiesel production, can be reacted further to commodity-oxygenated chemicals via either catalytic hydrogenolysis or oxidation. This work investigates the hydrogenolysis of sorbitol and glycerol and the oxidation of glycerol.

Materials and Methods

Hydrogenolysis reactions were conducted in a 300 mL stirred autoclave (Parr). Typical aqueous reaction conditions were 10 wt% sorbitol (Alfa Aesar) or 1-10 wt% glycerol (Acros Organics), a Ru/C (5 wt%, Acros Organics) or Pt/C (3 wt%, Aldrich) catalyst, 473-498 K, and a 40 bar H₂. When necessary, the pH was controlled using either CaO (Fisher Scientific) or NaOH (Mallinckrodt). A bimetallic PtRu/C was also tested for the hydrogenolysis of glycerol. This catalyst was prepared by the method of catalytic reduction [3]. The catalyst dispersions were measured by H₂ chemisorption.

Glycerol oxidation reactions were conducted in a 50 mL stirred autoclave (Parr). Typical aqueous reaction conditions were 0.3 M glycerol, 0.6 M NaOH, 10 atm O₂, at 308 or 333 K. Monometallic Au samples investigated were two World Gold Council catalysts (0.8 wt% Au/C and 1.5 wt% Au/TiO₂) and a 0.5 wt% Au/activated-carbon catalyst prepared by Au sol deposition. A series of AuPd/C bimetallic samples were prepared by the catalytic reduction method [3], starting with a Pd/C (3 wt%, Aldrich) parent catalyst. Particle sizes for the catalyst were determined by TEM. Products of the hydrogenolysis and oxidation reactions were analyzed by high performance liquid chromatography.

Results and Discussion

Initial studies on the hydrogenolysis of sorbitol and glycerol have shown that under basic conditions at 473 K and 40 bar H₂, Pt/C is approximately 5 times more active than Ru/C. In the presence of both catalysts, a non-reactive lactate salt formed via a solution-mediated pathway dominated product selectivity. Under neutral conditions, Ru/C was 5 times more active than Pt/C for the hydrogenolysis of glycerol (TOF_{Ru/C} = 0.04 s⁻¹), however the activity was almost an order of magnitude less than that at high pH and otherwise identical conditions.

No lactate salt was observed under neutral conditions; instead propylene glycol and gas phase products dominated the product distribution. Ru/C promoted the formation of methane whereas Pt/C promotes the formation of carbon dioxide. The selectivity of bimetallic PtRu/C catalysts was similar to that of the monometallic Ru/C catalyst.

The rate of glycerol oxidation at 333 K was significantly higher over a Au/C (TOF = 17 s⁻¹) than over a Pd/C (TOF = 0.6 s⁻¹). However, the Pd/C sample had a higher selectivity to glyceric acid. The observed C-C cleavage that leads to glycolic acid is attributed to H₂O₂ formed during the oxidation reaction over Au. A reaction pathway accounting for all observed glycerol oxidation products over the monometallic Au catalyst is proposed. Results from XAS indicated a high degree of Au-Pd interaction for the AuPd/C bimetallic catalysts. The AuPd catalysts revealed similar TOFs to that of a monometallic Au catalyst, indicating that the Pd simply helped disperse the Au atoms. The higher selectivity to glyceric acid that was observed over the AuPd catalysts is currently being investigated.

Significance

This work proposes a reaction pathway involving peroxide intermediates during the oxidation of glycerol over Au catalysts.

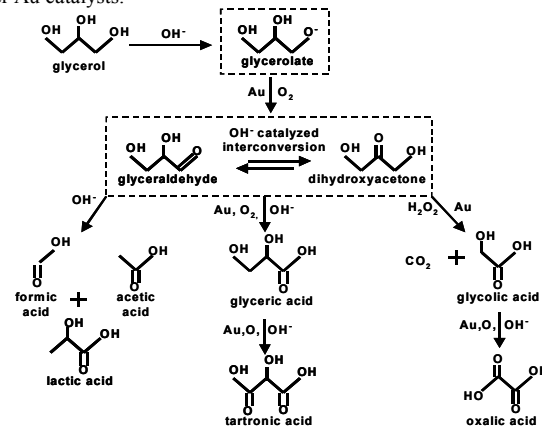


Figure 1. Proposed reaction pathway for the aqueous phase oxidation of glycerol over supported Au catalysts in the presence of a strong base. Species within boxes are proposed intermediates that were never directly isolated.

References

1. Committee on Biobased Industrial Products, National Research Council, "Biobased Industrial Products: Research and Commercialization Properties" p. 109. National Academy Press, Washington, D.C., 2000.
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3. Barbier, J., Marecot, P., Del Angel, G., Bosch, P., Boitiaux, J.P., Didillon, B., Dominguez, J.M., Schifter, I., and Espinosa, G. *Appl. Catal. A: General* 116, 179 (1994).