Catalytic Oxidation of Glycerol to High-Value Chemical Dihydroxyacetone

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Introduction

With increasing biodiesel production, large amounts of glycerol are obtained as byproduct, in a 1:10 ratio with biodiesel, resulting in its price decrease from 43 to 13 cents/gallon in the last three years. To maximize the economics of biodiesel production, it is essential to devise methods to utilize the byproduct glycerol. We use glycerol as feedstock for the oxidation reaction, which can produce a range of valuable fine chemicals as shown in Figure 1. The most important of these oxygenates is dihydroxyacetone (DHA), valued at ~$20/lb. To-date, DHA has been used mainly as a sunless tanning agent in the cosmetics industry and as a food additive, but it also has other potential large-scale uses.

Materials and Methods

Catalytic oxidation of glycerol to DHA was conducted in the presence of bismuth promoted platinum catalyst, supported on activated carbon (Pt-Bi/C). The bimetallic catalyst was optimized for Pt/Bi ratio, metal loading, structure and morphology, and support type. Various characterization techniques (BET, XRD, SEM, TEM, EDXS, XPS, etc.) are used to understand the catalyst structure and morphology that yield the best performance. With the optimum catalyst, the intrinsic kinetics of glycerol oxidation will be studied in a semi-batch reactor. The obtained kinetics will be used to develop a reactor model, which will be applied to identify the optimal operating conditions for maximizing the DHA yield using a membrane reactor (for related results involving a different reaction, see [1]).

The Pt-Bi/C catalyst was prepared using the co-impregnation method. Bismuth chloride (Aldrich) and chloroplatinic acid hydrate (Aldrich) were dissolved in HCl solution. The solution was then added dropwise into water immersed activated carbon (Aldrich, 20-40 mesh) while stirring. After co-impregnation, the catalyst precursor was washed, dried, calcined and reduced.

Glycerol oxidation was conducted in a semi-batch reactor (Parr). The screening experiments were conducted at 70 °C and 100 psig pressure. The product analysis was performed using an Agilent 1100 series HPLC, and an Agilent Carbohydrate column with UV and IR detectors.

Results and Discussion

To determine the effect of catalyst loading, four different catalysts with identical Pt/Bi ratio were prepared and tested. The results, shown in Figure 2, indicate that 4%Pt-2%Bi/C exhibits the best catalytic performance. Thus, for this support, the catalyst loading will be fixed at 4 wt% platinum and the Pt/Bi ratio changed to identify the optimal value which maximizes DHA yield at high glycerol conversion (i.e. simultaneously high conversion and selectivity). The variations in the support characteristics (pore size and distribution, pore volume, surface area, etc.) will also be investigated next and optimized.

Significance

DHA is a fine chemical widely used in the cosmetics, biological and chemical industries. Currently, it is produced from glycerol fermentation, but the conversion and selectivity are low [2]. The catalytic oxidation of glycerol to DHA is a promising alternative approach [3]. However, fundamental research on catalyst optimization, intrinsic reaction kinetics, and reactor modeling and optimization, has never been conducted previously for this reaction network and is the subject of the present work.

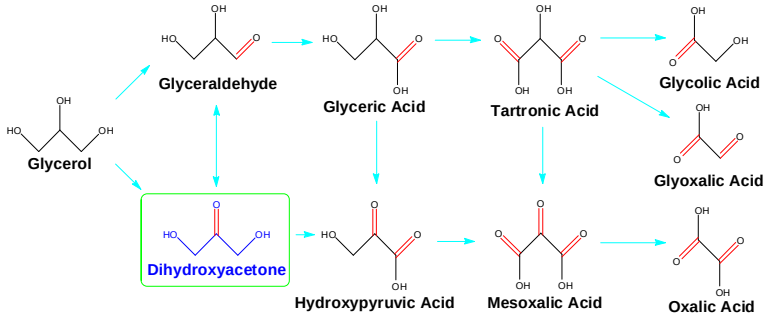

Figure 1. Glycerol oxidation network

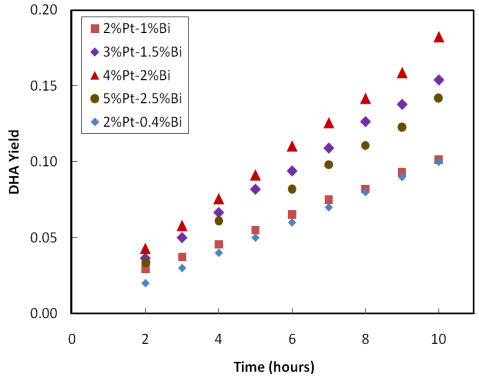

Figure 2. Effect of catalyst loading on DHA yield. 175 ml 10 wt. % glycerol solution in water, air flow rate 400 ml/min, 1.5g catalyst, temperature 70°C, 100 psig pressure.

References

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3. Kimura, H., Tsuto, K., Wakisaka, T., Kazumi, Y., and Inaya, Y. *Appl. Catal. A: General* 96, 217 (1993).