

Selective oxidation of glycerol over Pt/SBA-15 promoted by Bismuth

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Abstract: Selective oxidation of glycerol was conducted over Pt-Bi/SBA-15 catalyst with loadings of 0-3 wt% bismuth. In the presence of bismuth, dihydroxyacetone (DHA) was mainly formed (60% selectivity at 94% conversion) through oxidation of secondary hydroxyl group in glycerol at 348 K. The yield of DHA was increased with increasing bismuth loading up to 0.3 wt% and then almost constant when bismuth loading was further increased. The activity and selectivity of Pt-Bi/SBA-15 was comparable to those on the physical mixture of Pt/SBA-15 and Bi(NO₃)₃•5H₂O. Glyceric acid (GLA) was found to be able to leach Bi⁰ into solution and form complex with Bi⁰ or/and Bi³⁺ during the oxidation.

Keywords: Bismuth, Dihydroxyacetone, SBA-15.

1. Introduction

As a biomass derivate, glycerol has long been attracting much attention due to its ample supply after the booming of bio-diesel industry. Utilization of glycerol to produce more value-added chemicals is of high interest not only because of its high availability, but also its versatile chemical structure with three functionalized –OH groups. DHA, primarily used in cosmetic industry, is the secondary alcohol oxidation product of glycerol, and it is commercially produced in a fermentation process with a relatively low glycerol concentration and long operating time¹.

Since Kimura et al² first reported the chemical synthesis of DHA directly from glycerol using platinum-bismuth bimetallic catalyst, there have been many studies focused on improving the catalytic activity with Bi addition for high yield of DHA. Ning et al³ in their work reported that Pt catalyst with Bi in solution could selectively catalyze the glycerol to DHA with comparable performance of preloaded Bi-Pt catalyst. In this work, SBA-15 was applied as the support. Time course and effect of various content of on the catalytic activity were investigated.

2. Experimental (or Theoretical)

SBA-15 was synthesized through sol-gel method. Pt-Bi/SBA-15 was prepared by impregnating the H₂PtCl₆ and Bi(NO₃)₃•5H₂O with SBA-15. After 2 h impregnation, the mixture was dried, followed by reduction under 573 K with 10 ml/min H₂ flow rate for 2 hour. The obtained catalysts were denoted as xPt-yBi/SBA-15, where x and y denote the loading of Pt and Bi (wt%).

Oxidation experiments: A total of 0.1 g catalyst was added together with 1 ml 1 M glycerol into the tube reactor. After introduction of 4 ml water and 1 atm O₂, the reaction was started at 348 K temperature. When reaction ended, 1 mmol of 1,4-BDO and 1 mol DMF were added as internal standard substances, respectively, prior to GC & HPLC analysis.

3. Results and discussion

The conversion of glycerol was gradually increased with increasing reaction time (Fig.1). In the case of Pt-Bi/SBA-15, DHA was mainly formed accounting for 60% of glycerol conversion with 56.1% yield. On the other hand, GLA was formed as a dominant product on Pt/SBA-15 and the yield of DHA was quite low (ca. 4%). These results clearly showed that the formation of GLA was strongly inhibited by bismuth.

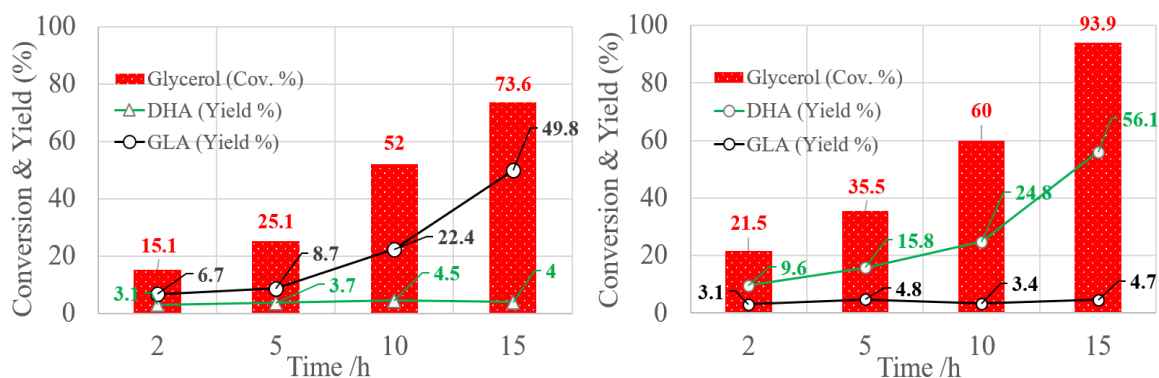


Figure 1. Glycerol oxidation over: 1) left, 3Pt/SBA-15; 2) right, 3Pt-0.3Bi/SBA-15. Conditions: 1 mmol glycerol, 5 ml H₂O, 0.1 g catalysts, 1 atm O₂, 348 K.

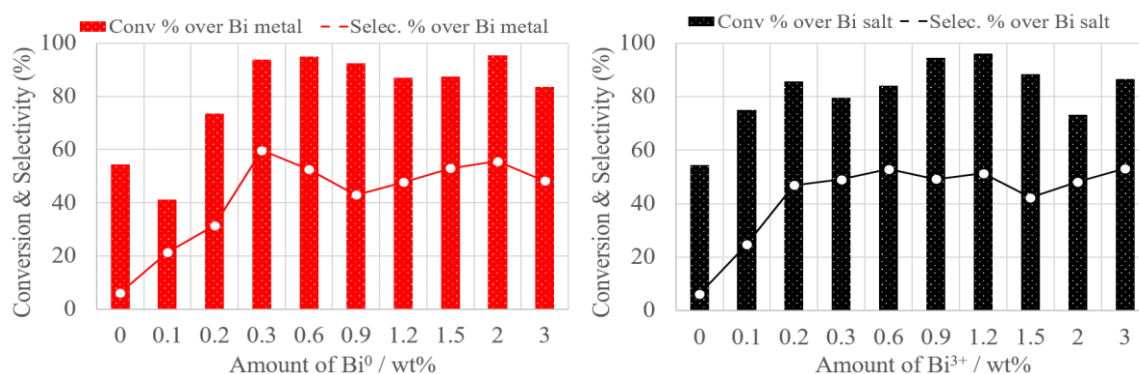


Figure 2. Oxidation of glycerol over: 1) Red bar, Pt-Bi/SBA-15; 2) Black bar, Pt/SBA-15+Bi(NO₃)₃. Conditions: 1 mmol glycerol, 5 ml H₂O, 0.1 g catalysts, 3 wt% Pt, 1 atm O₂, 348 K, 15 h.

Both the yield of DHA and conversion of glycerol were increased with increasing bismuth loading up to 0.3 wt% and then almost constant when bismuth loading was further increased (Fig. 2). Interestingly, the activity and selectivity of Pt-Bi/SBA-15 was comparable to those on the physical mixture of Pt/SBA-15 and Bi(NO₃)₃•5H₂O, indicating that the addition of bismuth enhanced the catalytic performance of Pt/SBA-15 regardless of modification method of Bi species. Leaching behavior was examined in some alcohols and carboxylic acid including glycerol, formic acid, glycolic acid, GLA etc. We found that GLA, which possesses carboxylic and α -hydroxy groups, was responsible for the leaching of Bi⁰ into solution. This suggests that dynamic equilibrium of Bi between Pt surface and GLA has an influence on the inhibition of the formation of GLA, resulting in the improvement of the selectivity to DHA.

4. Conclusions

Selective oxidation of glycerol to DHA proceeded on Pt-Bi/SBA-15 catalyst, although GLA was mainly formed on Pt/SBA-15. The activity and selectivity of Pt-Bi/SBA-15 was comparable to those on the physical mixture of Pt/SBA-15 and Bi(NO₃)₃•5H₂O. Moreover, GLA, with carboxylic and α -hydroxy groups, was responsible for the leaching of Bi⁰ into solution. Based on these results, we proposed that dynamic equilibrium of Bi between Pt surface and GLA has an influence on the inhibition of the formation of GLA, resulting in the improvement of the selectivity to DHA.

References

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