

Mechanism of glycerol hydrogenolysis to 1,2-propanediol over Cu(111) and CuCr₂O₄(100)

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The catalytic reaction of glycerol hydrogenolysis is one of the most attractive routes since it is efficient and alternative route to conventional fossil fuel-based route for the production of 1,2-propanediol (1,2-PDO). 1,2-propanediol is a value-added chemical, which is widely used as an antifreeze agent, a solvent for colouring, a monomer in polymer industry [1].

Many catalysts, such as Rh, Pt, Cu, etc., have been reported on for the reaction [2,3]. Among them, it is well-known that Cu-based catalysts exhibit superior performance, and have economical advantage. Although some of catalysts have been somewhat successful from an aspect of catalytic performance, there is lack of fundamental understanding for mechanism of glycerol hydrogenolysis over Cu-based surfaces. This can be an obstacle for rational design of new catalysts.

Herein, the reaction mechanism of glycerol hydrogenolysis to 1,2-PDO on Cu(111) and CuCr₂O₄(100) surfaces using Density Functional Theory (DFT) calculations.

First of all, we compare the adsorption behaviors of glycerol on both surfaces (Fig. 1). For the both cases, metal-oxygen interactions are confirmed to be dominant. However, on CuCr₂O₄ surface, hydroxyl groups of glycerol interact with Cr atom rather than Cu atom, leading to shorter bonding distance Cr-O than Cu-O. Consequently, more stable adsorption of glycerol is found on CuCr₂O₄(100) than Cu(111).

Three mechanisms have been proposed for the glycerol hydrogenolysis into 1,2-PDO; dehydration-dehydration-hydrogenation,

dehydration-hydrogenation, and direct glycerol hydrogenolysis. Among them, dehydration-hydrogenation mechanism is generally accepted over Cu-based catalysts [4]. According to the mechanism, dehydration reaction is considered as a rate-determining step. Therefore, activation energies for OH cleavage step of glycerol over the surfaces were calculated. From the results, not only the detailed mechanisms of the reaction but also origins of different catalytic behaviors of the surfaces were investigated.

In addition to the dehydration step, the hydrogenation reaction as a second step of hydrogenolysis was also investigated over Cu(111) and CuCr₂O₄(100) surfaces. From the comprehensive calculations for whole reaction, CuCr₂O₄ surface provide more stable adsorption sites for reactant and intermediates than Cu surface. The roles of Cu and Cr atoms on CuCr₂O₄(100) were also revealed.

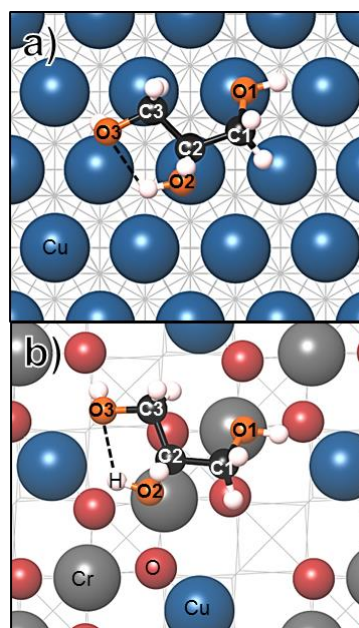


Fig.1 Top view of most stable configurations of glycerol on a) Cu(111) and b) CuCr₂O₄(100)

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