Selective catalytic oxidation of glycerol to synthesize 2-Dihydroxyacetone

Pachpande CP, Waghmare JS

Department of Oils, Oleo chemicals & Surfactants Technology, Institute of Chemical Technology, Mumbai-19, E-Mail: pachpandec@yahoo.com

Received 10 June; accepted 16 August; published online 01 September; printed 16 September 2013

ABSTRACT

Glycerol is a by-product from biodiesel industry. Biodiesel production is increasing exponentially. So the crude glycerol generated has also been generated in a large quantity. This glycerin can be utilized in many applications viz. pharma, personal care, etc industry. Glycerin refinery price goes much higher such that it is not convenient for small scale biodiesel producers. Oxidation of glycerin yields various specialty products. And selective oxidation yields the compounds having particular functional groups. Platinum–bismuth bimetallic catalyst gives selective results for oxidation. In this selective reaction various percentage of glycerin is taken as initial reactant and their ratios to catalysts are studied across the parameters. These results give the yield in percentage conversion of glycerol to dihydroxyacetone.

Keywords: Oxidation, Bimetallic catalyst

Abbreviation: DHA - Di hydroxy acetone

To Cite This Article:
Pachpande CP, Waghmare JS. Selective catalytic oxidation of glycerol to synthesize 2-Dihydroxyacetone. Discovery Science, 2013, 5(15), 44-46

1. INTRODUCTION

Now a day crude oil prices are going to be higher and higher. Therefore there is a good replacing is required for these fuel. The developing countries are going to launch biofuels. It will help economy as well as agriculture also. Biofuels burns cleaner than petroleum fuels. And this leads to reducing global warming. Biodiesel is going to replaceable fuel for petroleum diesel. But there are several issues are increasing the final cost of biodiesel. One of these issues is disposal of crude glycerin produced extensively. Glycerol (sometimes called glycerin) is the name of the commercial product consisting of glycerol and a small amount of water. Glycerol is actually trihydric alcohol CH (OH), which is more accurately named 1,2,3-propanetriol. Structure is shown as Figure 1.

Catalysis

Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all biological reactions require catalysis. Furthermore, catalysis is the most important technology in environmental protection. The term “catalysis” was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions. He assumed that catalysts possess special powers that can influence the affinity of chemical substances.

2. LITERATURE

In 2004 production of biodiesel was about 3,000,000 tons. Approx 380,000 tons of additional glycerol was available, almost double the present requirement (Joseph B. Gonsalves et al 2006). As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetables oils has also been generated in a large quantity. Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics, and many other industries, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers. Many research projects and studies have been conducted and innovative utilizations of the crude glycerol are under investigations. It will be beneficial to the research community as well as biodiesel industry in understanding the progress of glycerol for value-added applications and for reference in manipulating their own integrated plans for sustainable and profitable biodiesel production (Naresh Pachauri et al). There are many products can be derived from glycerol viz syngas, hydrogen gas, acrylic acid, acetonitrile, propanediols, glycerol esters, ethers, epichlorohydrin, dihydroxyacetone etc. The present discussion focuses selective oxidation of glycerol to synthesize dihydroxyacetone. The oxidation products of glycerol are as given in Figure 2.

The components derived from glycerol are valuable intermediates for fine and specialty chemicals and some of them are useful as such (Ullman Encyclopedia). Their current and common production methods involve complex organic syntheses, fermentation and multiple step reactions and the production costs are high and amounts of produced waste are large. Selective catalyzed reactions from glycerol offer benefits in reduced productions costs, increased selectivity and reduced amounts of waste and solvents. Studies are concentrated on heterogeneous catalysis and supported platinum and palladium are regarded as the best catalysts for glycerol oxidation. The DHA (di hydroxy acetone) is the current issue of this literature. The performance of the monometalic

Figure 1

1,2,3-propanetriol

Pachpande et al.
Selective catalytic oxidation of glycerol to synthesize 2-Dihydroxyacetone,
Discovery Science, 2013, 5(15), 44-46,
www.discovery.org.in/ds.htm

www.discovery.org.in
© 2013 Discovery Publication. All Rights Reserved
It is noted that, for supported Pd and Pt catalysts, the addition of OH⁻, as NaOH, increases the conversion of glycerol. However, for Au/C catalysts, the presence of OH⁻ is essential to observe any glycerol oxidation. It is proposed that, in the absence of a base, the initial dehydrogenation of glycerol, via H-abstraction, which must be the first step in the oxidation process, is not possible for the Au/C catalyst and is slow for the Pd/C and Pt/C catalysts (Silvio Carrettin et al). In one green chemistry journal it is criticized that the acid media favors glyceraldehydes, while in basic media DHA selectivity is more, as given as Figure 3.

Corrado Crotti et al had done selective dehydrogenation of glycerol to DHA. The reaction is achieved under iridium-catalyst, base-free hydrogen transfer conditions by the appropriate selection of catalyst. In this all of the organ iridium derivatives examined for hydrogen transfer reaction from glycerol to all the acceptors tested. With the use of ketones and defins, only low conversions were observed, whereas the choice of benzaldehyde as the hydrogen acceptor significantly raised the reaction conversion. DHA once more proved to be an evasive molecule due to its propensity to undergo thermal degradation, thus decreasing the actual yield of the reaction (Corrado Crotti et al. 2010). Kinetic study of glycerol oxidation has work out by Wenbin Hu and team. In this work the used catalyst 3%Pt-0.6%Bi/C to achieve higher selectivity of DHA. Turnover rate of DHA formation has been plotted against time of reaction. The surface energy required for desired product synthesis has been calculated. But they obtained maximum DHA yield 31.2% (Wenbin Hu et al). Liquid support catalyst using gold as oxidizing agent was studied by S. Demirel-Gülen and group. The effect of the support of different carbons was studied and no glycerol conversion could be detected where as gold nano particles supported on different carbons (carbon black, activated carbon and graphite) and oxides (TiO₂, MgO and Al₂O₃) were active. The various parameters have been determined by varying, e.g. catalyst amount, stirring speed and NaOH/glycerol ratio. Activation energy required for selective oxidation of glycerol is determined (Demirel-Gülen et al 2005). Also Two types of catalysts were recognized: the first, characterized by well-dispersed nanoparticles with a mean diameter centered at 6 nm, that did not maintain the initial selectivity of the oxidation through to full conversion; the second, characterized by larger particles (> 20 nm), that, on the contrary, maintained constant selectivity from the beginning to the reaction end (Francesca Porta et al 2004). Rígis García et al preliminary study shows that, depending upon the reaction conditions and upon the nature of the catalyst, it is possible to orientate the selectivity of glycerol. This proven that platinum catalyst gives more oxidation of primary hydroxyl group in glycerol, hence there is a need of promoters (Régis Garcia et al 1995). Kimura et al investigated the catalyst which gives better efficiency for selective oxidation of glycerol. These experiments include oxidation reaction along with different oxidizing catalysts viz. Pd, Au, Re, Ru. Here they found for this case Pt is most suitable catalyst. Also the work includes various promoters viz. Bi, Te, Pb, Sb and Se. It is experimentally found that 3% Bi loading on 5%Pt on carbon is better for this reaction (Hiroshi Kimura et al 1993).

3. CONCLUSION

It is seen that platinum catalyst gives better performance to oxidize glycerol. But selective oxidation of secondary position of glycerol is incorporated with bismuth metal. Hence platinum- bismuth bimetallic catalyst on carbon or charcoal is favorable to synthesize dihydroxyacetone from glycerol. The percentage of platinum is from 3% to 10% and for bismuth it is from 0.5% to 1.5% depending upon process parameters.
REFERENCES


11. Silvio Carrettin, Paul McMorn P Johnston, Ken Griffin, Christopher J Kiely, Gary A Attard, Graham J Hutchings. Oxidation of glycerol using supported gold catalysts. Department of Chemistry, Cardiff University, UK; Johnson Matthey, UK; Department of Materials Science and Engineering, Lehigh University, Bethlehem, USA.

12. Ullman, Encyclopedia of industrial chemistry, vol 11; page 11190


14. Wenbin Hu, Brian Lowry, Arvind Varma. Catalytic oxidation of glycerol to dihydroxyacetone. School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA