Chapter 13
Valorisation of Glycerol to Fine Chemicals and Fuels

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ABSTRACT

The selective transformation of biomass-derived compounds to useful fine chemicals and fuels has developed rapidly in recent years, and biomass compounds will soon become one of the main resource contributors for the production of chemicals. In the near future, it is expected that biomass derived compounds will contribute substantially to global chemical production along with fossil-based analogues. Although, there is still debate about the sustainability of the usage of biomass-derived molecules, it is important to emphasise that effort has been made to use biomass in the most efficient way, and that the biomass resources used are not suitable for food purposes. In this review we will focus to present selected examples on the transformation of glycerol in three distinct areas; (i) glycerol oxidation, (ii) glycerol hydrogenolysis and (iii) glycerol aqueous reforming, using supported metal nanoparticles as the chosen catalysts.

1. INTRODUCTION

The selective transformation of biomass-derived compounds to useful fine chemicals and fuels has developed rapidly in recent years, and biomass compounds will soon become one of the main resource contributors for the production of chemicals, (Alonso, Wettstein, & Dumesic, 2012; Corma, Iborra, & Velty, 2007; Vennestrom, Osmundsen, Christensen, & Taarning, 2011). In the near future, it is expected that biomass derived compounds will contribute substantially to global chemical production along with fossil-based analogues. Although, there is still debate about the sustainability of the usage of biomass-

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derived molecules, it is important to emphasise that effort has been made to use biomass in the most efficient way, and that the biomass resources used are not suitable for food purposes. A few important examples from the current literature that have shown effective ways of transforming biomass-derived molecules to useful chemicals and fuels are: (i) cyclodehydration of sugars, leading to furan-type products, with subsequent further transformation of these intermediates yielding more useful compounds such as levulinic acid and γ-valerolactone, which can be used as platform chemicals (Chheda, Roman-Leshkov, & Dumesic, 2007), (ii) hydrogenolysis of sugars to yield ethylene and propylene glycols, and (iii) glycerol valorisation to fine chemicals and fuels, such as acrylic acid, 1,2-propanediol, glyceric acid, hydrogen and methanol production. Figure 1 shows the common reactions used to obtain high value products from glycerol. In this review we will focus to present selected examples on the transformation of glycerol in three distinct areas; (i) glycerol oxidation, (ii) glycerol hydrogenolysis and (iii) glycerol aqueous reforming, using supported metal nanoparticles as the chosen catalysts.

2. SELECTIVE OXIDATION OF GLYCEROL

The valorisation of glycerol is an emerging area that has been extensively studied in recent years (Chheda, Huber, & Dumesic, 2007; Rahmat, Abdullah, & Mohamed, 2010; Zhou, Beltramini, Fan, & Lu, 2008), with a large body of this research focusing on the oxidation of glycerol to fine chemical products. The selective oxidation of glycerol can provide a range of useful fine chemical products used in pharmaceutical and perfume industry (Figure 2). A range of the presented catalysts developed for this oxidation are often also used to for the oxidation of interrelated polyols such as ethylene glycol, 1,2-propanediol (Dimitratos, Lopez-Sanchez, Meenakshisundaram, et al., 2009; Prati & Rossi, 1998) and 1,3-propanediol (Dimitratos, Lopez-Sanchez, Meenakshisundaram, et al., 2009; Biella, Castiglioni, Fumagalli, Prati, & Rossi, 2002; Taarning, Madsen, Marchetti, Egeblad, & Christensen, 2008).

Many research groups have focused on the optimisation of catalytic performance of materials that are able to tune activity and selectivity to the desired products. Therefore, glycerol oxidation is one of the most extensively studied reactions in recent years, and as such it can provide insights into the design and synthesis of new catalysts, covering a wide range of materials, such as nanomaterials, multicomponent oxides and heteropolyacids, (Beltran-Prieto, Kolomaznik, & Pecha, 2013; Sheldon, 2014). Glycerol is a by-product from biodiesel production, (Bharathiraja et al., 2014) and due to the fact that it is a highly functionalised molecule a large number of products can be formed from glycerol oxidation, (Rampino, Kavanagh, & Nord, 1943; Pagliaro, Ciriminna, Kimura, Rossi, & Della Pina, 2007). The first step for glycerol oxidation involves the formation of dihydroxyacetone under acidic conditions or glyceraldehyde under alkaline conditions. Sequential oxidation can subsequently lead to the formation of glyceric acid and tartronic acid as a product of the subsequent oxidation of glyceric acid. Formation of mesoxalic acid could occur due to the successive oxidation of tartronic acid. C-C cleavage products such as, glycolic, glyoxylic oxalic and formic acids could form depending on the experimental conditions. Therefore minimising C-C cleavage and enhancing the selectivity to desired products such as acids or to the corresponding aldehyde or ketone is a highly challenge. One of the main solutions for this challenge is the design of catalysts with specific properties, to allow control of activity and selectivity to the desired product. One of the main classes of catalysts used for the oxidation of glycerol are supported metal nanoparticles.