Oxidation of bio-renewable glycerol to value-added chemicals through catalytic and electro-chemical processes

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HIGHLIGHTS

• A review on catalytic and electro-catalytic oxidation of glycerol.
• Various catalytic synthesis methods have been evaluated.
• Different physico-chemical characteristics of catalysts have been evaluated.

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ABSTRACT

Due to its unique structure, characteristics, and bio-availability, glycerol transformation into value-added chemicals has been in the spotlight in recent years. This study provides a comprehensive review and critical analysis on catalytic and electro-chemical oxidation of glycerol into commodity chemicals, which have broad applications to the pharmaceutical, polymer, and food industries. Various synthesis methods (e.g. impregnation, sol-immobilization, incipient wetness, and deposition precipitation) for the preparation of the catalysts are discussed. Catalytic performance of mono-, bi-, multi-, and non-metal supported catalysts on carbon black, activated carbon, graphene, single- or multi wall-carbon nano-tubes, layered-double hydroxides, metal oxides, and polymers are evaluated. Among the methods, sol-immobilization is highly commended since fine metal NPs could be homogeneously distributed on the support, reported as an effective factor for controlling the selectivity of the desired product. In particular, the environmentally benign novel polymeric structures, illustrate significant breakthroughs in production of commodity chemicals compared to the conventional materials. Homogeneous oxidation of glycerol by enzymes and microorganisms also displayed acceptable performance particularly in production of DHA, but at the expense of long reaction time. Unlike the homogenous and heterogeneous catalytic processes, electro-chemical oxidation could be tuned for high product selectivity by controlling the nature, composition and structure of the electro-catalyst as well as the electrode potential. Most importantly, combination of electro-chemical oxidation of glycerol with oxygen or water reduction process in full- and electrolysis-cells, respectively could be the ultimate goal in this field. Simultaneous generation of value-added chemicals and electrical energy would have significant economical and environmental merits compared to the conventional processes. The current state-of-the-art of the glycerol oxidation process and recommendations for further research are also included.

1. Introduction

Petroleum exploitation and its cracking to simple hydrocarbons in the early 20th century is the most important breakthrough to industrialization. Fossil fuel has been our main source of energy for approximately a century. The current oil production rate reaches to about 12 Mt/day and it is predicted that its demand will increase significantly to around 16 Mt/day by 2030 due to the significant increase in the world’s population and rapid industrial development [1,2]. Therefore, various types of environmental concerns such as massive

Abbreviations: GLYLD, glyceraldehyde; GLYCA, glyceric acid; TARA, tartronic acid; TAR, tartronate; GLA, glycolic acid; GA, glyoxylic acid; HPYA, hydroxypropyruvic acid; OXALA, oxalic acid; MOXA, mesoxalate; FA, formic acid; LA, lactic acid; PAL, pyruvaldehyde; Mt/day, million tonnes per day; GLY, glycerate; CA, chron-oamperometry; CV, cyclic-voltammetry; ACA, acetic acid

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discharge of CO₂ and even the depletion of fossil fuel resources have become the main agenda in upholding sustainability. Indeed, cheap supply of fossil fuel (less than 100 USD/barrel) will no longer be available by 2040 [3]. Consequently, there have been many attempts to replace fossil fuels with renewable energy. Biomass and biofuels are alternative energy sources from renewable energy that could meet the huge energy demand and at the same time reduce environmental problems. The new term “bio-refinery” is used to describe the process for converting biomass to food, fuel, and value-added chemicals. Indeed, bio-refineries could significantly reduce the energy demand, CO₂ emission, and moderately lower the operating costs [4].

Biodiesel, is one of the most important and valuable alternative liquid biofuels in the transportation sector. Biodiesel is environmentally friendly, technically feasible and biodegradable [5]. Plant lipids and animal fats (biomass) are common sources of biodiesel. Compared with traditional diesel fuels, the utilization of biodiesel can reduce 70% hydrocarbons and 50% particulate matters on exhaust emissions [United States Environmental Protection Agency (US EPA)], and net 78% CO₂ emissions [6]. Application of non-edible oils have attracted much attention recently. Researchers who compared the benefits of waste-to-energy technologies, including incineration, anaerobic digestion, and biodiesel reported that the production of biodiesel using scum sludge was the most economic scenario, creating an added value of US $491,949 and US $610,624/year. Also, it is reported that approximately 15.784 million USD/year and environmental gains in the form of carbon credits can be saved for a city (Metropolitan Region of Campinas, São Paulo State, Brazil) if waste frying oil is collected and utilized to produce biodiesel [7]. Life cycle assessment is a widely used methodology for quantifying and examining the environmental aspects of biodiesel. The analysis of well-to-wheel (WTW) carbon footprint of biodiesel helps determine to what extent its widespread implementation can enable a country to reach its GHG reduction targets. As a result, the GHG emission per unit energy of the biodiesel at nominal values for the process parameters was found to be 360 g e-CO₂/MJh. If solar energy is utilized to increase the biomass concentration from 20 to 31 wt %, the GHG emission of the algae-derived diesel is reduced to 273 g e-CO₂/MJh. Indeed, biodiesel production is environmentally viable and policies and incentives should ideally support research, development, and commercialization for this process [8].

The EU Energy and Climate Change Package (CCP) became operative on April 6, 2009, which was reported the EU goals for 2020: a reduction of 20% in greenhouse gas (GHG) emissions compared to 1990; an improvement of 20% in energy efficiency (compared to forecasts for 2020) and a 20% share of renewable energy in the total European energy mix. Part of the latest 20% share, is represented by a 10% minimum target for biofuels in the transport sector to be achieved by all Member States [9]. Thus, due to enormous advantages of biodiesel, different countries around the world have devised plans to enhance their biodiesel production. For instance, United State produced more than 2.7 ×10⁷ gallons biodiesel in 2009. The U.S. biodiesel industry has reached a key milestone with more than 1 billion gallons of biodiesel production in 2011 [10]. In addition, it is estimated that global biodiesel market will significantly expand to 45 billion liter by 2020 by an average growth rate of 42% per year [11].

Biodiesel production opens a spectacular opportunity for bio-refinery since glycerol is the main by-product in the transesterification process. Indeed, 1 mol of glycerol is formed for every 3 mol of biodiesel produced. Glycerol is listed as one of the top 12 most important bio-based chemicals in the world and is predicted to become the major chemical for future bio-refineries [12]. It is expected that the global surge in biodiesel production in 2020 could produce over 41.9 billion liter of crude glycerol [13]. Application of glycerol for the synthesis of value-added chemicals has directly cut the cost of biodiesel production by half from 0.63 to 0.35 USD per liter [14,15]. In addition, ethanol production from glycerol could reduce production costs by almost 40% (no steam-explosion needed) when compared with production from conventional corn-derived bioethanol. Moreover, if fuels and reduced chemicals are targeted together, there are many advantages for using glycerol over sugars, (the most commonly used fermentation substrate), which might translate into higher yields and lower capital and operational costs. In fact, converting glycerol to pyruvate generates twice the amount of reducing equivalents produced from glucose or i.e. xylose [16].

Prior to 1999, glycerol was mostly produced from fatty acids (47%), soaps (24%), fatty alcohols (12%), and biodiesel industry (9%). However, biodiesel industry has become the main glycerol producer (64%) since 2009 [17]. Thus, glycerol consumption is expected to increase significantly by 50% in 2018. In fact, its consumption is estimated to expand from 2000 kt in 2011 to approximately 3070 kt in 2018 with revenues of 2.1 $ billion [18].

Glycerol purity is the key component for its industrial applications. The conventional method to produce biodiesel is from vegetable oil with homogeneous (acid or base) catalyst. Inevitably, the glycerol produced during the conventional process will include impurities such as water, methanol, residual catalyst, free fatty acids, un-reacted mono-, di- and tri-glycerides, methyl ester and various organic and inorganic compounds (matter organic non-glycerol (MONG)) [19,20]. Consequently, low quality glycerol requires different purification and treatment steps to reach the > 95% purity for feedstock in industrial refineries. However, the purification processes are costly and some industries prefer to burn the impure glycerol as waste material and use refined (> 98.5%) glycerol instead of purified crude glycerol. As a result, more than 150 to 250 thousand tons of crude glycerol was wasted in 2006 and 2007 [21,22].

Majority of researchers have used heterogeneous catalysts and non-edible oils for higher quality biodiesel and glycerol production. For instance, Bournay et al., [23] used Zn-Al heterogeneous solid catalyst in a continuous process to produce high quality biodiesel (98.3%) and glycerol (98%). Indeed, their catalytic process could totally avoid all the costly treatment and purification processes for direct application of crude glycerol in industries.

Glycerol is edible, bio-sustainable, non-toxic, easily available and has a multi-functional structure. Thus, glycerol can be used as a renewable source of value-added chemicals (more than 2000 products) in various reaction pathways [20,23,24]. Also, the primary and secondary hydroxyl groups that consist in glycerol molecules are susceptible to various chemical reactions, namely hydrolysis, esterification, dehydration, etherification, oxidation, pyrolysis, transesterification, oligomerization, polymerization, and carboxylation. Table 1 lists all the catalytic processes and products that can be produced from glycerol. Among these possibilities, the oxidation of glycerol is considered to be one of the most important chemical routes to produce aldehydes, carboxylic acids, and ketones, frequently used in the preparation of new chemicals for cosmetics, medicine or food industry purposes. The most important valuable oxygenates are glyceraldehyde (GLYLD), dihydroxycetone (DHA), glycric acid (GLYCA), hydroxypropyric acid (HPYA), tartaric acid (TARA), mes-oxalic acid (OXALA), glycolic acid (GLA), and glyoxylic acid (GA). However, glycerol conversion and selectivity for a specific product vary according to the reaction conditions (temperature, concentration of reactants, solvent used, ratio of glycerol and catalyst, mass-transfer conditions) and type of oxidation. In addition, reactor configuration, nature of support, relationship between rate of product desorption and subsequent oxidation to other glycerol derivative, and the selection of a specific oxidation method, which implies the use of a specific catalyst, microorganisms, chemical reagents or electro-chemical conditions could also affect the activity.

Fig. 1 depicts the glycerol oxidation mechanism. Oxidation of primary hydroxyl groups of glycerol produces TARA and GLYCA. The DHA or keto-malonic acid is produced by oxidation of the secondary hydroxyl groups of glycerol. On the other hand, OXALA is produced by oxidation of all three glycerol hydroxyl groups [25,26]. Although some of the glycerol oxidation products are highly valuable and expensive such as OXALA and TARA, others like DHA have lower market price.
The majority of these products can be used as intermediate materials to synthesize novel polymers and fine chemicals. For instance, DHA is significantly used in the cosmetic industry as a safe skin tanning agent and TARA is used as a drug-delivery agent, particularly to increase the absorption of tetracycline antibiotic into blood [27,28]. Unfortunately, all these valuable chemicals are produced only in a small scale due to their costly and contaminated production processes. Indeed, hazardous oxidizing agents such as permanganate, nitric acid, and chromic acid are used during the oxidation process.

However, glycerol characteristics serve great opportunities for application of different heterogeneous catalysts with clean and cheap oxidizing agents such as oxygen, air, and hydrogen peroxide (H2O2) in oxidation reaction. Hence, glycerol oxidation reaction can be performed in an electro-chemical process or in the presence of heterogeneous supported metal, homogenous and bio- catalysts [28]. Nevertheless, the main concerns of oxidation reaction are selectivity of the desired products, increasing catalytic activity, stability of catalyst against poisoning, and minimizing the application of alkaline environment [18]. Some of the most important factors that give significant impact on the desired products selectivity are reaction temperature, pH of the solution, size of the metal particles, support characteristics and metal nanoparticles (NPs) (e.g. Au, Pd, Pt). Among the reported factors, the textural and physico-chemical characteristics of the supports seem to have profound influence on catalyst activity and products distributions [29].

Based on the importance of glycerol as one of the top 12 materials in the chemical industry and the significant impact of products that can be produced from glycerol on human’s life, the number of research studies on glycerol has significantly increased recently. Fig. 2 clearly indicates that the number of studies on glycerol has doubled in the last 10 years. The two review papers available in this field were published more than 5 to 6 years ago; the first one is only based on electro-chemical oxidation of glycerol [24], and the second one is a short review [30]. Unfortunately, the two review papers could not properly address application of various types of catalysts, the importance of supporting materials, and application of various catalytic synthesis methods related to glycerol oxidation. Thus, a comprehensive review on glycerol oxidation to valuable chemicals is imminent.

The main aim of this review is to evaluate and examine recent novel breakthroughs in glycerol oxidation process, particularly with the focus...
on catalytic (heterogeneous and homogenous) and electro-chemical processes in alkaline and base-free environments. In addition, the review addresses the critical knowledge gaps for enhancing high conversion and selectivity in glycerol oxidation. Also, the pervasive influence of the physico-chemical characteristics and preparation methods of various metal-supported catalysts on the selectivity of desired products will be discussed comprehensively. As a result, the catalytic glycerol oxidation studies will be classified into four subsections of mono-, bi-, multi-, and even non-metallic supported catalysts. Metallic catalysts for the oxidation of the primary hydroxyl group are usually based on Au, Pt, and Pd NPs [25,31,32]. Pd and Pt are characterized based on the lowest hydrogenolysis activity of Group VIII metals with good hydrogenation and dehydrogenation activities maintained. However, alcohol oxidation in aqueous phase using Au as catalyst is more selective and less prone to metal leaching and deactivation caused by over-oxidation and self-poisoning by strongly adsorbed by-products compared to Pt and Pd [33].

Generally, factors that have been evaluated as the most influential parameters on the glycerol oxidation reaction conversion, product distribution, product selectivity, and catalyst long-life stability are (1) NaOH presence in reaction medium, (2) different catalyst preparation methods such as impregnation, sol-immobilization, incipient wetness, and deposition precipitation, which could control the particle size of metal NPs, (3) basic or acidic characteristics of support, (4) influence of sample structure on modification of metal NPs, (5) presence of capping agents, and finally (6) application of bi- and multi-metallic NPs instead of mono-metallic ones. Table 2 summarizes some of the results from previous studies on catalytic oxidation of glycerol over different metal supported catalysts. Selective oxidation of glycerol into fine chemicals have used different supported mono-, bi-, multi- and even non-metallic catalysts. Metal catalysts for the oxidation of the primary hydroxyl group are usually based on Au, Pt, and Pd NPs [25,31,32]. Pd and Pt are characterized based on the lowest hydrogenolysis activity of Group VIII metals with good hydrogenation and dehydrogenation activities maintained. However, alcohol oxidation in aqueous phase using Au as catalyst is more selective and less prone to metal leaching and deactivation caused by over-oxidation and self-poisoning by strongly adsorbed by-products compared to Pt and Pd [33].

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2. Catalytic oxidation of glycerol

The heterogeneous catalytic oxidation of glycerol with molecular oxygen is considered to be one of the most attractive methods for production of glycerol derivatives. Selective oxidation of glycerol into fine chemicals have used different supported mono-, bi-, multi- and even non-metallic catalysts. Metal catalysts for the oxidation of the primary hydroxyl group are usually based on Au, Pt, and Pd NPs [25,31,32]. Pd and Pt are characterized based on the lowest hydrogenolysis activity of Group VIII metals with good hydrogenation and dehydrogenation activities maintained. However, alcohol oxidation in aqueous phase using Au as catalyst is more selective and less prone to metal leaching and deactivation caused by over-oxidation and self-poisoning by strongly adsorbed by-products compared to Pt and Pd [33].

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Table 2
Catalytic oxidation of glycerol over different supported catalysts in the basic and base-free environments.

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Con (%)a</th>
<th>Sel (%)b or Y (%)c</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic Environment</td>
<td>Mono-metallic based</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1%Au/charcoal</td>
<td>12 mmol GLY/20 mL H2O, 333 K, 3 h, 12 mmol NaOH, O2 (0.3 Mpa)</td>
<td>56%</td>
<td>100 (SGLYAC)</td>
<td>[34]</td>
</tr>
<tr>
<td>2</td>
<td>1%Au/C</td>
<td>0.3 M GLY, NaOH/GLY = 4 (mol/mol), 303 K, 20 h, O2 (0.3 Mpa)</td>
<td>100%</td>
<td>92 (SGLYAC)</td>
<td>[35]</td>
</tr>
<tr>
<td>3</td>
<td>Au/C</td>
<td>1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 3 h, O2 (0.1 Mpa)</td>
<td>30%</td>
<td>75 (SGLYAC)</td>
<td>[36]</td>
</tr>
<tr>
<td>4</td>
<td>Au/C</td>
<td>1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 3 h, O2 (0.1 Mpa)</td>
<td>50%</td>
<td>81 (YDHA), 26 (YHYPAC)</td>
<td>[37]</td>
</tr>
<tr>
<td>5</td>
<td>Au/C</td>
<td>A 50 cm³ batch reactor; 333 K, 0.5 MPa O2</td>
<td>50</td>
<td>83 (SGLYCA)</td>
<td>[38]</td>
</tr>
<tr>
<td>6</td>
<td>Au/AC</td>
<td>1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 1 h, O2 (0.3 Mpa)</td>
<td>100%</td>
<td>60 (SGLYAC)</td>
<td>[39]</td>
</tr>
<tr>
<td>7</td>
<td>Au/AC</td>
<td>1.5 M GLY, NaOH/GLY = 2 (mol/mol), 333 K, 1 h, O2 (0.3 Mpa)</td>
<td>30%</td>
<td>66.3 (SGLYCA)</td>
<td>[40]</td>
</tr>
<tr>
<td>8</td>
<td>Au/TiO₂</td>
<td>A 50 cm³, batch autoclave, 333 K, 1 MPa O2</td>
<td>83</td>
<td>61 (SGLYCA)</td>
<td>[41]</td>
</tr>
<tr>
<td>9</td>
<td>Au/TiO₂</td>
<td>A continuous fixed-bed reactor, 333 K, 1 MPa O2</td>
<td>32</td>
<td>37 (SGLYCA)</td>
<td>[42]</td>
</tr>
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<td>10</td>
<td>Au/TiO₂</td>
<td>323 K, glycerol/metal = 1000/1, 300 kpa O2</td>
<td>98</td>
<td>73 (SGLYCA)</td>
<td>[43]</td>
</tr>
<tr>
<td>11</td>
<td>Au/Al₂O₃</td>
<td>30 mmol min⁻¹ O₂</td>
<td>77</td>
<td>30 (SGLYCA)</td>
<td>[44]</td>
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<td>12</td>
<td>Au/Nb₂O₅</td>
<td>333 K, NaOH/glycerol = 3, H₂O₂</td>
<td>66.1</td>
<td>66.3 (SGLYCA)</td>
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<td>333 K, NaOH/glycerol = 2, 6 bar O2</td>
<td>93</td>
<td>45 (SGLYCA)</td>
<td>[46]</td>
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<td>50 (SGLYCA)</td>
<td>[47]</td>
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<td>333 K, NaOH/glycerol = 2 mol/mol, 5 bar O2</td>
<td>100</td>
<td>45 (SGLYCA)</td>
<td>[48]</td>
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<td>16</td>
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<td>64</td>
<td>69 (SGLYCA)</td>
<td>[49]</td>
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<td>17</td>
<td>Au/C-G</td>
<td>298–373 K, 1–8 bar O2, 7 h</td>
<td>100</td>
<td>56 (SGLYCA)</td>
<td>[50]</td>
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<td>Au/C</td>
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<td>100</td>
<td>36 (SGLYCA)</td>
<td>[51]</td>
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<td>100</td>
<td>60 (SGLYCA)</td>
<td>[52]</td>
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<td>20</td>
<td>Au/MWCNT</td>
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<td>50 (SGLYCA)</td>
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<td>333 K, NaOH/glycerol = 2 mol/mol, 3 bar O₂</td>
<td>93</td>
<td>47 (SGLYCA)</td>
<td>[54]</td>
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<td>333 K, NaOH/glycerol = 4, 5 bar O₂, 2.5 h</td>
<td>99</td>
<td>60 (SGLYCA)</td>
<td>[55]</td>
</tr>
<tr>
<td>23</td>
<td>Au/Al₂O₃</td>
<td>10% GLY, 333 K, 30% NaOH, 5 h, air (0.1 Mpa)</td>
<td>100%</td>
<td>70 (SGLYCA)</td>
<td>[56]</td>
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<td>100</td>
<td>60 (SGLYCA)</td>
<td>[57]</td>
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<td>Cu)</td>
<td>333 K, NaOH/glycerol = 2 mol/mol, 3 bar O₂</td>
<td>90</td>
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<td>Cu)</td>
<td>333 K, NaOH/glycerol = 2 mol/mol, 3 bar O₂</td>
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<td>Cu)</td>
<td>333 K, NaOH/glycerol = 2 mol/mol, 3 bar O₂</td>
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<td>333 K, NaOH/glycerol = 2 mol/mol, 3 bar O₂</td>
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(continued on next page)
Table 2 (continued)

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<th>No</th>
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<th>Sel (%) or Y (%)c</th>
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<td>Au-Pt/TiO2</td>
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<td>Pt-Bi/charcoal</td>
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<td>1:0.5Au-Rh-C2</td>
<td>323 K, NaOH/Glycerol = 1 mol/mol, &lt; 6 nm particle size, 0.3 Mpa O2</td>
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<td>Au-Cu/Co/ZrO</td>
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<td>79 (S GLYCA)</td>
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<td>HPW-MCM-48</td>
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<td>Au-SiO2</td>
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<td>61 (S S)</td>
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<td>Au-Pt/TEGO</td>
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<td>Pt/MWCNT</td>
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<td>68</td>
<td>Pt/Sb/MWCNT</td>
<td>150 mL min⁻¹ O2, Temperature 333 K; time 2 h</td>
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<td>51 (S S)</td>
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<td>69</td>
<td>1%Pt/CNT</td>
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<td>70</td>
<td>1%Pt-0.65%Sn/CNT</td>
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<td>30.8 (S GLYCA), 10.9 (S S)</td>
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<td>Pt@C/MWCNT</td>
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<td>Pt-NPs/HT</td>
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<td>Pt/Fe3O4/Ppy</td>
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<td>55 (S GLYCA)</td>
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<td>70 (S S)</td>
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<tr>
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<td>74 (S GLYCA)</td>
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<td>Not active</td>
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<td>LDH-[Cr(SO3-salen)]q</td>
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<td>HPMo-V2O4</td>
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<td>82</td>
<td>PdPb/Al2O3</td>
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<td>83</td>
<td>Au-Pd/PT/TiO2</td>
<td>373 K, 24 h, substrate/metal = 2728/1</td>
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<td>64.1 (S GLYCA)</td>
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<td>84</td>
<td>Cu (II)-Mg-Al (LDH)</td>
<td>333 K, 4 h, Ph = 7, 3% H2O2</td>
<td>40.3</td>
<td>40.3 (S S)</td>
<td>[99]</td>
</tr>
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</table>

a Conversion.  
b Selectivity.  
c Yields to the particular product given in parentheses.  
d Au based carbon nano-spheres catalyst.  
e Au/Graphen sample which synthesized by gold-sol (SGT) method.  
f Au/MWCNT thermal treatment at 900 K.  
g Au/MWCNT synthesized through the “sol immobilization” technique.  
h 5% H2 as reducing agent in Al2O3 catalyst.  
i THPC as reducing agent in Au/Al2O3 catalyst.  
j THPC as reducing agent in Au/Al2O3 catalyst.  
k Fixed bed reactor.  
l 2%PtSn1/C-R, catalyst supported on the activated carbon (C) and reduced (R) at 300 °C with H2.  
m Cx-yB, x, y, weight % of Pd and Bi loaded on resin and “B” means reduced by Borohydride (BH4).  
f Pd nanoparticles within a nitrogen-containing covalent triazine framework (CTF).  
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supported catalysts. Research studies are classified in this table similar to this review content. Indeed, all the studies are divided in two main groups of basic and base-free environments and each section included mono-metallic, bi-metallic, multi-metallic, and other catalysts sub-sections. This table provides a spectacular opportunity for comparison of the researches in various conditions. For instance, Rodrigues et al. [57] findings were totally different over Pt/C/MWCNT (SGLYCA = 67%) compared to the main product (SGLYCA = 60%) over the Au/MWCNT [38,49]. Indeed, the impact of noble metals on the obtained desired products could be clearly seen from these results. Also, Ribeiro et al. [58] compared the catalytic activity of mono- (Pt or Pd) and bi-metallic (Pt-Cu) based catalysts supported on CNT in both basic- and base-free environments. The results are reported in the rows number 30, 31, 36, 71, 72, and 79 of Table 2. In detail, mono-metallic Pt/CNT and Pd/CNT samples showed clear results of high activity in the basic environments with about 88–90% conversion compared to the very low activity in the base-free environment. Particularly, Pd/CNT was totally not active in base-free environment. Similarly, more than 90% glycerol conversion and 56% SGLYCA were obtained over the bi-metallic (1%Pt-0.65%Cu/CNT) in the basic environment, while GLYCA selectivity dropped to less than 15% at < 40% reaction conversion in the base-free environment. In fact, the significant impact of basic- and base-free environments are clear in this study, thus we should separate different researches based on the environment that they studied. As mentioned before, another significant factor in the synthesis method. Lei et al. [88] compared (rows 69 and 70 Table 2) the catalytic activity of Pt/AC mono-metallic sample which synthesized by application of polyols (PO) and incipient wetness impregnation (IWI) techniques. As results, the former techniques showed significant improvement in selectivity of desired products (35% SGLYCA and 15.7% SGLYCA) at 55% reaction conversion, while the IWI method led to the dramatic fall in reaction conversion (18.8%) and about 40% reduction in products selectivities. Finally, Zhang et al. [96] proposed that the glycerol oxidation to FA could be the substitute of conventional reforming process for producing H2 due to its lower energy requirement but higher yield and selectivity.

2.1. Glycerol oxidation in alkaline medium

Hosts of homogeneous and heterogeneous catalytic oxidation of glycerol studies have been performed in an alkaline environment. The presence of an alkaline medium was demonstrated to favor glycerol deprotonation, the first step in the oxidation process, considered essential for the oxidation of the primary alcohol [25,31,100]. In fact, the importance of alkaline environment in the oxidation reaction has been evaluated by many research groups.

Yuan et al. [34] reported that the activity and selectivity of Au catalysts in enabling the oxidation reactions particularly for polyl oxidation, depends critically on the co-presence of a base (usually NaOH, or in essence OH−) [76]. For instance, glycerol oxidation using various supported Au NP catalysts showed quite high yields of GLYCA in the presence of highly basic (molar NaOH/GL > 1) conditions, but exhibited no activity without NaOH [59]. Basic OH is usually considered to be an initiator or promoter for alcohol/polyol activation by abstracting a proton from the hydroxyl or one of the hydroxyls in the substrate alcohol/polyol molecules [100]. The presence of alkaline medium impacts not only the activity, but also the selectivity of catalysts in the aerobic oxidation of alcohols/polyols. Thus, any further understanding of the catalytic chemistry would be impossible without unravelling the effects of NaOH alone on the reactivity and product selectivity of alcohols/polyols in the aerobic oxidations. The results revealed that glycerol consumption rate employing NaOH alone (without Au catalyst) is 5–70 times lower than the rates in the co-presence of Au and NaOH catalysts. However, the GL consumption rate employing only Au catalyst in NaOH-free solution (i.e., without co-presence of NaOH) was even several times slower than the rate employing NaOH alone, which highlights importance of the co-presence of Au and NaOH for the oxidation reaction.

As a result, in a catalytic cycle, the base catalyst (OH−) could initiate the reaction by attacking the H of the hydroxyl group to produce an anionic complex [R1R2CHOH−OH]−, in which the O−H bond of the hydroxyl group becomes lengthened and weakened (Fig. 3). An O2 molecule would then react with the H of the R1R2CH skeleton via the transition state TS1, in which the C−H bond of R1R2CH is weakened. At this TS1 of 2-PO oxidation, the C−H bond is increased to 1.26 Å, while the O−H bond is 1.41 Å. Via the TS1, the O2 molecule becomes activated, with the formation of OOH−, and the H atom in the hydroxyl group transfers to the catalyst OH, yielding a H2O molecule and a ketone product. The as-formed OOH− would also react with H2O to generate a H2O2 and a OH− (the catalyst), entering another catalytic cycle. A second channel leading to alcohol oxidation would be opened by the reaction between H2O2 and [R1R2CHOH−OH]− to form another ketone product via TS2 as the transition state. Also, it is reported that O2 closes the catalytic cycle by serving as an electron scavenger and regenerating hydroxide ions that are consumed in the reaction to produce aldehyde intermediates and acid products [100]. The key elementary steps for the two reaction channels are summarized below:

\[ \text{Channel I: } R_1R_2CHOH + OH^- \rightarrow [R_1R_2CHOH−OH]^- \] (1)
\[ [R_1R_2CHOH−OH]^- + O_2 \rightarrow R_1R_2CO + OOH^- + H_2O \] (2)
\[ \text{Channel II: } OOH^- + H_2O \rightarrow H_2O_2 + OH^- \] (3)
\[ [R_1R_2CHOH−OH]^- + H_2O_2 \rightarrow R_1R_2CO + OH^- + 2H_2O \] (4)

Among these elementary steps, the R1R2C−H bond breaking owing to the O2 attack (Eq. (2)) is the rate-determining step that possesses the highest barrier.

2.1.1. Mono-metallic catalysts

2.1.1.1. Au-based catalysts. Undoubtedly, mono-metallic supported catalysts on various types of supports are the most popular heterogeneous catalysts reported in the glycerol oxidation reaction. Application of mono-metallic Au supported on three different carbons namely graphite (G, 10 m2/g), ribbon-type carbon nano-fiber (CNF-R, 109 m2/g), and carbon nano-spheres (CNS, 3 m2/g) was reported for oxidation of purified and crude glycerol in liquid phase [45]. The initial results revealed that the highest glycerol conversion and GLYCA selectivity were obtained over Au/CNS sample and crude glycerol was not completely oxidized even after 7 h. Meanwhile the commercial glycerol reached about 45% GLYCA selectivity at 100% glycerol conversion after 7 h. Au/CNS sample had many open edges at the surface due to the presence of the “unclosed” graphitic layers, to facilitate high chemical reactivity, due to the small size of Au particles. In fact, the CNS pore sizes are approximately ≤ 6 nm, while the size of the Au particles (4.2 nm) and the molecular size of glycerol (0.62 nm) are smaller than CNS pore sizes. Thus, the active sites can be located in the approximately small pores of CNS, generating a strong steric effect causing the molecules to be more likely confined favoring the oxidation of primary alcohol group of glycerol.

In another attempt, the synthesis of different types of Au supported carbon metal (AC, G, and three types of CNFs with different structures with respect to the arrangement of the graphitic planes of platelet (CNF-P), fishbone (CNF-F), and ribbon (CNF-R)) catalysts, prepared by two different approaches (impregnation (IMP) or gold-sol (SGT)), has been investigated by Gil et al., [101]. The characterization results revealed the distribution size of Au particle in Au/AC and Au/G samples were similar (8–12 nm). However, the Au size was different based on the nature of CNFs. In fact, the Au particle size was in the following order for the three different CNFs: Au/CNF-R (12–20 nm) < Au/CNF-F (22–25 nm) < Au/CNF-P (22–27 nm). The preparation method of catalyst has a significant effect on the activity. Indeed, samples prepared by SGT method exhibited higher glycerol conversion and GLYCA selectivity as compared to the samples prepared by IMP. This is evident

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when the Au/G-SGT sample completed the conversion in 400 min, but the Au/G-IMP managed to perform only 70% glycerol conversion within the same time. Approximately 50% of GLYCA selectivity was obtained from Au/G-SGT catalyst at 30% glycerol conversion. Generally, the catalyst activity is in the following order Au/G-SGT > Au/CNF-R > Au/CNF-F > Au/CNF-P > Au/AC. In fact, G, the most crystalline metal, promoted strong anchoring of small, thin, and faceted Au particles, to facilitate the proton abstraction from glycerol and increased the catalyst conversion.

The reaction mechanism for catalytic oxidation of glycerol using a quasi-homogenous solution of Au NPs, prepared by the Turkevich method, was investigated by Skrzynska et al. [48]. Their main focus was to determine glycerol oxidation reaction mechanism in the presence of Au NPs. Fig. 4 illustrates the obtained reaction pathway for glycerol oxidation over supported Au NPs catalyst. Red, blue, and green arrows correspond to simple oxidation, C−C cleavage reactions, and Cannizzaro reactions, respectively. Abbreviations CR and NCR stand for catalytic and non-catalytic reaction, respectively, whereas the “+” and “−” shows the extent favorability. In detail, there are two main possible pathways for the primary glycerol transformation. In the first possible route, glycerol can be directly oxidized to GLYCA, due to the highest observed selectivity of GLYCA at the initial stages and particularly it reached about 100% at lower temperatures. This reaction proceeds favorably in the presence of a catalyst, a base, and an excess of oxygen (CR+ + , NCR+). In the second possible reaction route, direct oxidative cleavage of glycerol to GLA and FA, probably through the formation of highly reactive radical-type species without intermediate formation of partially oxidized C3 products (e.g. GLYCA). The second possible route only requires the presence of a base and oxygen, while the presence of a catalyst seems not to be essential. Notably, in the absence of oxygen glycerol conversion is almost completely suppressed. Indeed, reaction conversion more than 0.5% cannot be obtained in the absence of oxygen and without the gold catalyst even by a base and high reaction temperature (e.g. 80 °C). Then, GLYCA can be split into GLA and C3 components, mainly formaldehyde (NCR+ + , CR+). The latter is supposedly immediately oxidized to FA by oxygen (CR+ + ) or is involved in the sequence of Cannizzaro-type cross-reactions. Further oxidation of GLYCA to TARA seems to proceed through the formation of HPYA (CR+ + ), which can easily undergo classical hydrolytic C−C cleavage (NCR+ + ). The last possible products (i.e., GA and OXALA) can be obtained by direct oxidation and/or oxidative cleavage reactions from both TARA and GLYCA. It seems that direct oxidation is favored in the presence of Au NPs, whereas high temperatures and strong basic conditions favor oxidative cleavage and straight hydrolytic transformations, such as: retro-aldol, α- and β-dicarbonyl cleavage, oxidative cleavage with CO2 evolution, and Cannizzaro cross-reactions.

The effect of thermal and chemical treatments on catalytic activity was evaluated by Rodrigues et al. [102,103]. In detail, they synthesized different types of mono-metallic (Au, Pt, Pd, Ir, and Rh) supported catalysts by application of thermal treatment in preparation of different types of ACs (AC0; NOTRIX ROX 0.8 activated carbon, AC1: oxidized AC0, AC10900: AC1 which is thermal treated at 400 °C, AC11900: AC1 which is thermal treated at 900 °C). In the first stage, some of the samples such as Pd/AC0, Rh/AC0, and even Au/AC0 (Au; Au catalyst prepared by sol-immobilization method with NaBH4 as reducing agent) reached > 90% glycerol conversion after 3 h at 60 °C. However, the catalytic activity of Rh/AC0 exhibited a downward trend by increasing the reaction temperature and pressure above 60 °C and 3 bar. As results, the Au mono-metallic sample was selected for further investigations in this study. In the second step, the ACs were prepared with different levels of acidity and basicity (various levels of oxygenated functional groups on the surface) by chemical treatment. Also, thermal treatment was used to improve the textural characteristics of the synthesized samples. As results, the Au/AC0, Au/AC10900 and Au/AC11900+H2 samples with basic supports (limited concentration of oxygenated groups) exhibited higher activity. Indeed, the thermal and chemical treatments significantly impacted the catalytic activity and stability.

Carbon materials have been proven to be a good catalytic support in liquid phase reactions due to their specific characteristics (e.g. acid and base resistance, porosity, surface chemistry control and the possibility of metal support) [81,104,105]. However, potential catalytic applications of carbon nano-structures such as carbon nano-tubes (CNT), CNF, and CNS is trending [106,107]. Some of the CNTs specifications such as high surface area, good physical and chemical stability, and excellent electronic properties have attracted much attention recently. In fact, external surface area of CNTs caused metal NPs to be highly exposed and accessible to reactants, which improves the efficiency of the synthesized catalysts. Modification of CNT properties by controllably placing defects or foreign atoms such as nitrogen (N) brings along tremendous technological implications [108,109]. As in other crystalline solid structures, the position of N in CNT network must not exclusively be substitutional to affect the properties of the structures. The properties of nano-scopic objects depend crucially on the position of each atom [110–112]. Bearing in mind that N contains one additional
electron as compared to C, novel electronic properties can be expected if N atoms directly substitute C atoms in the graphitic lattice and one could anticipate that they would generate an n-type material [113].

Gil et al. [114] synthesized three types of nitrogen-dopped carbon nano-spheres (CNSB (thermal pyrolysis of benzene), CNSAN (thermal pyrolysis of aniline), CNSNB (thermal pyrolysis of nitrobenzene)) as a support for Au NPs for selective oxidation of glycerol to GLYCA. The synthesized catalysts had the following particle size of Au/CNSB (4.2 nm) < Au/CNSAN (10.5 nm) < Au/CNSNB (13.1 nm). The Au/CNSB with the smallest and well dispersed Au NPs reached to a high metal-support interaction due to its high electrochemically accessible surface and high electron density. As a result, the Au/CNSB reached the highest activity with 68% GLYCA selectivity at 35% glycerol conversion after 1 h. Finally GLYCA selectivity reached to about 50% at 100% glycerol conversion after 400 min at 60 °C.

Fig. 5 clearly illustrates that textural and chemical characteristics of
support could influence the catalytic activity and selectivity. Indeed, based on the glycerol molecular size (0.620 nm), it is evident that a strong steric effect could be generated resulting in a well-confined form of the glycerol molecules that favored the oxidation of the primary alcohol group of glycerol (Fig. 5a). Nevertheless, in the case of Au/CNS\textsubscript{AN} and Au/CNS\textsubscript{NH}, the metal active sites were located on the surface of the supports (Fig. 5b). Consequently, the binding of glycerol over the Au surface is sufficient for oxidation of the secondary alcohol group of glycerol, requiring more space to react.

Rodrigues et al. [38,49–51] compared the catalytic activity of Au mono-metallic samples supported on multi wall carbon nano tubes (MWCNTs) and AC. The findings revealed that the distribution of products was totally different over Au/AC and Au/MWCNTs catalysts. The Au/AC led to the oxidation of primary hydroxyl group which cause more selectivity of GLYCA (60%), while Au/MWCNTs favored the oxidation of secondary hydroxyl group of glycerol and increased DHA selectivity (60%). High DHA selectivity over Au/MWCNTs sample could be due to the large mesoporous sample (MWCNTs). Results of thermal and chemical treatments of samples in this study were in a very good agreement with their previous findings, which is reported in Table 2, about the effectiveness of thermal treatment on improvement of catalytic activity [102,103].

Metal oxides are the second common supports after carbons, which are using in the preparation of heterogeneous catalyst for glycerol oxidation reaction. In the selection of particular metal oxide as a support, two utmost characteristics to be considered are strong metal support interaction (SMSI) and unique reversible interaction with several reagents.

TiO\textsubscript{2} is one of the favorite metal oxides used as a support in catalytic oxidation of glycerol. Dimitratos et al. [115] evaluated the effect of weight ratio of PVA/Au, Au concentration, heat treatment, and selection of support (TiO\textsubscript{2} or C) on the catalyst activity. Sodium borohydride and polyvinyl alcohol (PVA) were used for improving the pore size and distribution of Au NPs. The characterization results revealed that by controlling Au concentration and PVA/Au ratio, well-defined NPs with an average diameter of 3–5 nm could be fabricated. In fact, the increase of PVA/Au ratio reduced the average Au particle distribution in the Au/C sample. Also, higher Au concentration could reduce the effect of PVA/Au ratio on the Au particle size. However, the Au average particle diameter surged in the Au/TiO\textsubscript{2} supported sample when increasing the PVA/Au ratio at high Au concentration. The Au/C catalyst was the highest active sample with 73% selectivity to GLYCA and 79% glycerol conversion in the presence of the lowest (0.65 g) PVA/Au ratio. However, the Au/TiO\textsubscript{2} sample reached to 73.7% GLYCA selectivity at just 50% glycerol conversion with the narrowest particle size distribution (PVA/Au = 2).

Another metal oxide used as a support in catalytic oxidation of glycerol is SiO\textsubscript{2}. Kapkowski et al. [82] evaluated the efficiency of SiO\textsubscript{2}, Cu, and Ni and the use of Au NPs support in deep glycerol oxidation in a diluted and viscous liquid H\textsubscript{2}O\textsubscript{2}. Generally, the Au/SiO\textsubscript{2} samples appeared to be more reactive than Au/C sample while the Au/Cu and Au/Ni indicated good activity with 85.7% and 80.2% selectivities of acetic acid at 41.2% and 39.6% glycerol conversions. However, the two samples were destroyed due to leaching effect by Cu or Ni. However, the Au/SiO\textsubscript{2} sample reached to 90–99% acetic acid yield of complete glycerol conversion in the diluted aqueous glycerol solution. Although in a relatively viscous liquid phase these values decreased to 40% and 20%, the addition of acetonitrile could improve the acetic acid yield to 40%. Also, the 0.1%Au/SiO\textsubscript{2} sample exhibited the highest stability among synthesized samples. Complete conversion was attained in the first and second runs, however, the conversion dramatically dropped by 30% in the third run.

Lakshmanan et al. [116] compared two types of ceria-supported Au NPs catalyst preparation methods, which were chemical reduction with glycerol or conventional hydrogen-reduced method in selective oxidation of glycerol to LA. The initial finding revealed that the glycerol based chemical reduction approach led to synthesizing larger Au particles compared to the H\textsubscript{2} reduction method. The catalyst activity test of the 1%Au/CeO\textsubscript{2} reported larger Au average particle size, decreased the selectivity of GLYCA and surged the LA selectivity. Indeed, the 1% Au/ CeO\textsubscript{2} sample, prepared by chemical reduction method, and the Au particle average size of 6 nm conferred the highest LA selectivity of 83% at 98% glycerol conversion.

The increasing demand for high quality products seem to contradict with the needs to reduce all types of pollution during different manufacturing processes [117]. Environment friendly chemistry plays an important role in the design of novel catalysts [118]. In this regard, micro-encapsulation method has been recently recognized as a useful technique to immobilize metal catalysts onto polymers. In addition, it is an alternative strategy to enable safe handling, easy recovery, reuse and disposal at an acceptable economic cost [119,120]. The micro-encapsulation refers to the incorporation of an active substance in a shell or a matrix of a carrier component. The catalysts could be separated from a reaction mixture by simple filtration and recycled, making them suitable for green chemistry processes [121]. Despite all the recent efforts in this field, the described methods to prepare hierarchically complex Au micro/nano-structures constantly suffered from various issues (e.g. complex systems, tedious processes, difficult control of
particles’ size and shape, and lower reactivity of immobilized metal catalysts compared to the corresponding original catalysts) \cite{118,119}.

Gil et al. \cite{121} for the first time studied the synthesis conditions of micro-encapsulated (Au-PUF), which is Au NPs by in-situ polymerization of urea and formaldehyde (PUF) in the presence of an organic solvent (dimethyl sulfide (DMS)), supported on carbon black catalyst. Increasing amount of DMS from 0 to 35 mL reduced the Au encapsulation efficiency from 75 to 40%, while the Au particle size increased from about 120 nm to about 300 nm. The lower DMS amount caused smaller and better dispersion of Au particles with more homogeneous particle size distribution. The catalytic activity tests revealed that GLYCA selectivity increased by reducing the Au particle size, which showed the importance of catalyst preparation method to achieve better catalytic activity. In detail, the catalyst prepared using 30 mL DMS gave 12% GLYCA selectivity while the one with just 2.5 mL DMS attained 42.2% GLYCA selectivity.

Furthermore, Gil et al., \cite{117} evaluated the effect of different kinds of stabilizers or stabilization agents (cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyvinyl pyrrolidine (PVP), polyvinyl alcohol (PVA), and tetrakis (hydroxyl methyl) phosphonium chloride (THPC)) on the morphology, particle size of encapsulated Au, the Au particle size distribution and the encapsulation efficiency.

As results, the Au particle size and Au encapsulation efficiency increased in the following order MP.Au-CTAB (131 nm, 0.3 wt %) < MP.Au-SDS (135 nm, 0.7 wt%) < MP.Au-THPC (287 nm, 0.8 wt %) < MP.Au-PVP (339 nm, 1.1 wt%) < MP.Au-PVA (487 nm, 1.3 wt %). The catalytic tests results indicated that catalyst activity increased with decreased encapsulated Au particle size as follows: CTAB ~ DS > THPC > PVP > PVA. Therefore, catalyst with small and well dispersed metal particles and high metal surface exposition performed well. The MP.Au-CTAB and MP.Au-SDS reached quite similar glycerol conversion of 53% and 52% with 52% selectivity to GLA and about 40% selectivity to GLYCA. Fig. 6 shows a schematic diagram of the PUF micro particles formation process containing Au as a function of the stabilizer. When the stabilizer introduced into the system was cationic in nature (CTAB and THPC) an electrostatic attraction between AuCl₄⁻ ions and the positive charged head groups of the stabilizer took place. However, the anionic stabilizer (SDS) forced AuCl₄⁻ ions away from around their head groups, while, the non-ionic stabilizers (PVP and PVA) formed micelles with no apparent ionic charges, leading to a high incorporation of AuCl₄⁻ ions. In addition, the strong hydrophobicity of their long hydrocarbon chains, favored the stability of the micelles. Therefore, the concentration of AuCl₄⁻ ions into the micelle could be promoted. After the addition of the stabilizer, AuCl₄⁻ ions were reduced to Au metal using DMS (water-insoluble solvent). Au nuclei stabilized by stabilizer molecules began their growth stage. Subsequently, the solution of elemental Au was then added to the polymeric suspension, leading to the formation of PUF micro-particles containing Au.

Schunemann et al. \cite{122} reported quite different and novel route of visible-light-assisted process of glycerol oxidation using direct plasmonic photo-catalysis (DPP) process over two series of mono- and bimetallic Au supported catalysts. In particular, DPP is an appealing integrated system where plasmonic NPs act as both visible-light absorber
and active site for the chemical reaction [123,124]. An inherent benefit of DPP is the broader choice of applicable supports, as there is no limitation to light absorbing semiconductors, as in conventional plasmonic photo-catalysis. This allows the application of supports with desirable properties such as efficient pore confinement of metal NPs, high surface area, facile morphology control, abundance and cost efficiency. Initially a series of mono-metallic sample of Au supported on different types of SiO2 (Mono-dispersed mesoporous siliceous (MS), SBA-15, KIT-6, and MCM-41) tested in glycerol oxidation reaction and the 6%Au/MS sample showed the highest glycerol conversion of 33% in the presence of visible-light illumination compared to the other mono-metallic samples. Secondly, the increase of Au content from 6 wt% to 12.5 wt% surged glycerol conversion from 33% to almost 60%. The main reason for better activity of sample was SiO2 domains which caused homogenous distribution of Au NPs on the support (MS). Finally, the activity of 6%Au/MS sample was compared with a synthesized bimetallic Au–Cu sample. The activity test under visible-light illumination demonstrated an increase in Cu content from 0 wt% in the 6%Au/MS sample to 1 wt% in the 5%Au-1%Cu/MS catalyst increased the glycerol conversion from 18% to almost 45%, respectively. The DHA selectivity also increased from 80% to 90% in the presence of 6%Au/MS and 5%Au-1%Cu/MS catalysts, respectively.

2.1.1.2. Pt-based catalysts. Pt is the second noble metal which has been used in various chemical reactions such as glycerol oxidation. However, it is very expensive and strategic metal owing to its localized production regions (mainly in South Africa, Russia, Canada, and USA) [29]. Thus, many researchers try to reduce the Pt applications and improve its characteristics. Zhang et al. [124] investigated the application of four different bases (LiOH, NaOH, KOH, and Ba(OH)2) in selective oxidation of glycerol to LA over Pt/AC monometallic catalyst. Initial investigations in the presence of Pt/AC catalyst and base-free conditions confirmed the huge influence of basicity on the Pt/AC catalyst activity. The Pt/AC could reach 44.9% selectivity of LA at 58.5% glycerol conversion in the presence of NaOH at 90 °C. However, further investigation exhibited that application of LiOH significantly enhanced the LA selectivity to 69.3% at 100% glycerol conversion (T = 90 °C, LiOH/glycerol ratio = 1.5). The effect of various alkaline solutions on Pt/AC catalyst activity was as follows: Ba (OH)2 < KOH < NaOH < LiOH. The main reason for higher activity of Pt/AC in the presence of LiOH was due to the oxygen solubility in solution. In fact, when more oxygen is dissolved, the hydroxide ions regenerate faster and promote LA production.

The first heterogeneous monometallic Pt-NP based catalyst (Pt@C) stabilized by ethylene in glycerol oxidation to LA, was synthesized by Oberhauser et al. [125]. This approach curtailed the formation of oxidation products and ethylene acted as the hydrogen acceptor. Small Pt-NPs, generated by the metal vapor synthesis (MVS) technique, allowed the synthesis of size-tailored Pt NPs, regardless of the support. Indeed, the 1.5 nm sized Pt-NPs, generated by MVS and supported onto a high surface area carbon Ketjenblack (i.e., Pt@C), was easily stabilized against aggregation by high ethylene partial pressure (875 psi) during the reaction. Pt@C maintained its catalytic performance for a maximum duration of 780 h and LA chemoselectivity of 95% in three consecutive catalytic reactions.

The application of two types of Pt supported catalyst on both TiO2 nano-fiber (Pt/NF-TiO2) and TiO2 nano-powder (Pt/NP-TiO2) was evaluated by Chornaja et al. [126]. Higher glycerol/Pt ratio significantly reduced the glycerol conversion, while the increase in oxygen pressure from 1 to 6 atm enhanced the activity of the two catalysts. The 4.8%Pt/NF-TiO2 reached 63% GLYCA selectivity with a glycerol conversion of 100%. Meanwhile, the 4.8%Pt/NP-TiO2 reached 68% GLYCA selectivity with a glycerol conversion of 95% at the same optimal reaction conditions (0.3 mol/l glycerol feed concentration, 1.5 mol/l NaOH, glycerol/Pt ratio was 300 mol/mol, P(O2) = 6 atm at 60 °C).

In another study, Li and Zaera, [127] investigated the activity and selectivity of Pt/SiO2 catalyst as a function of Pt NPs size and shape. Three sets of samples were prepared. Two sets were functions of metal loading and prepared by impregnation using water (W) and ethanol (E) as solvent (Pt/SiO2-W and Pt/SiO2-E) while the third set used pre-made Pt colloidal NPs with specific size and shape (cub-octahedral (C) and tetrahedral (T)). For the first two groups of catalysts, samples which were made with ethanol displayed an overall better quality in terms of size and dispersion. The average Pt NPs size increased with metal loading. The Pt NPs size for the Pt/SiO2-W sample was in the range of 3.9–5.7 nm for 0.2 to 10 wt% Pt loading and for the Pt/SiO2-E samples it was in the range of 1.9–3.8 nm for the same amount of Pt loading. Also, the size dispersion was much narrower for the Pt/SiO2-E (0.3 nm) compared to Pt/SiO2-W (3 nm) sample.

On the other hand, the average NPs size of T-Pt/SiO2 and C-Pt/SiO2 NPs were 5.6 and 9 nm, respectively for the third series of synthesized samples. The activity tests revealed that the increase of metal loading did not only surged the metal NPs size but also enhanced both activity and chemical selectivity. In fact, larger NPs appeared to exhibit higher intrinsic activity and to favor oxidation at the terminal alcohols groups of the glycerol. Also, higher activity was observed with cub-octahedral Pt NPs compared to tetrahedral samples.

2.1.1.3. Pd-based catalysts. Pd is the third common noble metal which has been used widely in various chemical reactions such as glycerol oxidation to value-added chemicals. Hamid et al. [128] synthesized monometallic Pd catalyst supported on AC, hydrotalcite (HTc), and AC-HTc. The TEM characterization results revealed that the Pd NPs had an average size of 9.0, 9.1, and 11.2 nm on the HTc, AC, and AC-HTc supports, respectively. Also, CO2-TPD analysis exhibited that Pd/HTc sample possessed the highest concentration of basic sites compared to the other two samples. Meanwhile, the glycerol conversion and GLYCA selectivity increased in the following order: Pd/AC < Pd-HTc AC < Pd-HTc and Pd/HTc-AC < Pd/AC < Pd/HTc, respectively. Among all the tested catalysts, the Pd/HTc sample exhibited the highest GLYCA selectivity (80.4%) at 70.4% glycerol conversion. Higher basic sites and dispersion of Pd NPs are identified as the key factors for higher catalytic activity of Pd/HTc.

Application of various solvents (acetonitrile (CH3CN), dimethyl sulfoxide (DMSO), and CH3CN/H2O) and terminal oxidants (benzoquinone (BQ), air, O2) over Pd supported catalyst was investigated in selective oxidation of glycerol to DHA [129]. The catalytic oxidation of glycerol with 5 mol%Pd/C catalyst and in the presence of BQ and CH3CN reached to > 96% selectivity of DHA at 97% glycerol conversion at room temperature. However, by only a simple change in solvent from CH3CN to the mixture of CH3CN/H2O (7:1), 100% conversion can be obtained in just 3 h. Furthermore, the reaction was completed in only 15 min when DMSO was used as solvent. All these results revealed that solvent has a significant effect on the rate of oxidation reaction. Meanwhile, DHA yields of 69% and 73% were obtained in the presence of CH3CN/H2O solvent and 10 mol% Pd/C catalyst, respectively with the aid of O2 and air as the terminal oxidants.

The second most common metal oxide considered as a support in catalytic oxidation of glycerol is Al2O3. Chornaja et al. [130] investigated the use of monometallic Pd NPs supported on Al2O3, Y2O3, C, and Pyrex in the selective oxidation of glycerol to GLYCA. The initial activity revealed that 1.25%Pd/Al2O3 and 2.5%Pd/Al2O3 samples reached up to the highest selectivities of 66% and 74% for GLYCA at 70 and 74% glycerol conversions, respectively. However, other samples exhibited less than 53% glycerol conversion at 60 °C in 420 min.
of various Lewis acids (AlCl₃, CrCl₃, ZrCl₄, and FeCl₃) at different reaction temperatures (120 – 180 °C), O₂ pressures (0.5–1.5 Pa) for glycerol oxidation to FA. Initially, application of solely Ru(OH)₄/r-GO or FeCl₃ samples could not achieve more than 20% conversion. However, combination of Ru(OH)₄/r-GO and other four Lewis acids and combinations of Ru(OH)₄/r-GO with FeCl₃ recorded the best results with 53.5% yield of FA at 95.5% glycerol conversion.

Another metal oxide examined in glycerol oxidation was iron oxide. The first successful attempt was performed by Crotti end Farnetti, [132] They investigated application of various iron complexes with the polydentate ligand bis (2-pyridinylmethyl) amine (BPA) samples for production of DHA in the presence of H₂O₂ as oxidant. The initial activity tests indicated that Fe(OTf)₃ + BPA sample gave the highest glycerol conversion of 47% with 49% selectivity to DHA among all the tested Fe supported samples. However, further investigations revealed that only two products were produced (DHA and FA) in all the experimental runs. However, by tuning the experimental conditions, the highest glycerol conversion of 50% was achieved with complete elimination of FA and 100% selectivity to DHA. Further investigation recently by Farnetti and Crotti, [133] on iron salt (Fe(OTf)₃) revealed that about 98% FA selectivity and just traces of DHA and GLYCA obtained at about 20 times larger than Pd/C and 4 times larger than Au/C monometallic ones due to ensemble electronic bi-functional effects.

Farnetti and Crotti, [133] also found that only two products were produced (DHA and FA) in all the experimental runs. However, by tuning the experimental conditions, the highest glycerol conversion of 50% was achieved with complete elimination of FA and 100% selectivity to DHA. Further investigation recently by Farnetti and Crotti, [133] on iron salt (Fe(OTf)₃) revealed that about 98% FA selectivity and just traces of DHA and GLYCA obtained at about 20 times larger than Pd/C and 4 times larger than Au/C monometallic ones due to ensemble electronic bi-functional effects.

Jedsukontorn et al. [134] investigated the TiO₂-induced photocatalytic oxidation of glycerol in the presence of H₂O₂. They evaluated the effect of TiO₂ dosage (1–3 g/L), H₂O₂ concentration (0.3–1.5 M), light UV intensity (1.1–4.7 mW/cm²) and irradiation time (4–8 h). The activity tests revealed that TiO₂ and H₂O₂ in the presence of light UV-light gave very low glycerol conversion. However, the presence of all three components (TiO₂, H₂O₂, and UV-light) is essential to reach a good glycerol conversion and product selectivity. 71.25% GLA and 19.61% GLYCA selectivities at 71.4% glycerol conversion were obtained at 3 g/L TiO₂, 1.5 mol/L H₂O₂, and 4.68 mW/cm² light intensity after 8 h. Other efforts in the photo-catalytic partial oxidation of glycerol to DHA in water were performed by Maurino et al. [135] and Minero et al., [136] using Degussa P25 and Merck TiO₂ catalysts and their fluorinated derivatives. In fact, by using fluorinated Degussa P25 and very low concentration of glycerol (ca. 1 mM), almost 100% selectivity to DHA was obtained for conversions lower than 30% [134].

2.1.2. Bi-metallic based catalysts

As reported earlier, applications of bi-metallic catalysts in oxidation of glycerol to value-added chemicals have attracted much attention in the last decade. In fact, combinations of two metals, which one or both of them are noble metals could reduce the catalyst synthesis cost and improve the catalytic activity in the majority of cases. Also, bi-metallic samples could improve catalytic activity compared to the mono-metallic ones due to ensemble electronic bi-functional effects.

Improvement of catalytic activity in the presence of bimetallic catalysts conferred by Rodríguez et al. [137]. Using a series of Au-Pd/C bimetallic catalysts prepared by electro-less deposition (ED) in liquid phase and basic environment. In fact, Au was systematically and controllably deposited on the Pd surface of a monometallic Pd/C sample to form a series of catalyst with various surface composition of Au. The catalyst activity increased significantly by increasing the θAu value, which is the actual coverage of Au on Pd, to θAu = 0.5 where TOF was about 20 times larger than Pd/C and 4 times larger than Au/C monometallic samples. The higher activity of bimetallic sample could be attributed to ensemble electronic bi-functional effects or combination of these reasons. The highest catalytic activity (TOF = 2.3 s⁻¹) at θAu = 0.5 inferred both Pd and Au sites were involved in the rate determining step. Concerning product distribution, GLYCA selectivity remained approximately constant (80%) at 50% glycerol conversion for Au-Pd/C bi-metallic catalyst even by high Au coverage up to the θAu = 0.98. In fact, the result of this study was slightly better compared to the previous findings over mono- and bi-metallic catalysts of Pt and Au supports [38–50,107,125]. Also, Zhao et al. [138] reported, supporting Pd on Au surface eliminate undesired growth of Pd NPs and significantly reduced catalyst deactivation process during the glycerol oxidation reaction.

Mimura et al. [139] was one of the first groups to report synthesizing supported bimetallic samples on metal oxide (Au₀.83-Pd/TiO₂, Au₀.91-Pd/TiO₂, and Au/TiO₂). The Au/TiO₂ reached over 87% of the production yield (GLYCA, TARA, GLA), while Au₀.83-Pd/TiO₂ reached the highest yield (65%) of GLYCA among all samples tested. Evaluation of Pd effect on bimetallic samples activity exhibited that Au has an average diameter of 3.4 nm in Au monometallic sample. However, Au size increased to 7.1 nm in the Au-Pd bimetallic sample. The precise STEM characterization of NPs provide interesting results and the researchers concluded that the presence of Pd at the edge corner of the particles reduced the side reactions.

Application of bismuth (Bi) as promoter in the bimetallic catalytic oxidation of glycerol was evaluated by various researchers. Hu et al. [140] did a research on the sequential impregnation of Pt and then Bi, followed by NaBH₄ reduction for high glycerol oxidation rate. In addition, three types of activated carbons (AC1 (S BET = 600 m²/g, Dp = 4 nm); AC2 (S BET = 1200 m²/g, Dp = 2.2 nm); and AC3 (S BET = 1600 m²/g, Dp = 1.6 nm)) were used as support. Catalysts supported on AC2 and AC3 had higher Pt dispersion due to the larger surface area. However, the catalyst activity decreased when the support surface area increased. This may be explained from the average support pore size and molecular sizes of reactants glycerol (0.620 nm), H₂O₂ (0.027 nm), and O₂ (0.074 nm). In fact, the molecular size of glycerol, comparable to the average pore size of AC2 and AC3 supports, led to pore diffusion resistance. The optimum catalyst composition was determined to be 3 wt% Pt, 0.6 wt% Bi, supported on NoritDaroco 20–40 mesh AC1 to reach the maximum DHA yield of 48% at 80% glycerol conversion corresponding to 80 °C, 30 psig, and initial pH = 2.

Zhang et al. [141] evaluated the application of monometallic (Pt/AC) and bimetallic (Cu-Pt/AC) supported catalyst in selective oxidation of glycerol to lactic acid (LA). The bimetallic 0.5%Cu-1%Pt/AC sample exhibited the highest activity with 69.3% selectivity to LA at 80% glycerol conversion and 437 h⁻¹ TOF value, while the 1%Pt/AC only reached 56.6% LA selectivity at 40.6% glycerol conversion and 239 h⁻¹ TOF value at 90 °C in 4 h. The characterization results revealed that Cu could improve the dispersion of Pt on the support. The bimetallic samples possessed 2.3–3.5 nm average particle size compared to the 4.2 nm conferred by the monometallic catalyst. It was also found Cu could prevent the aggregation of some Pt-Cu interfaces. In addition, proper surface Pt/Cu molar ratio (0.62) and the presence of Cu⁺ and Cu²⁺ species also had vital roles in glycerol conversion and LA selectivity enhancement. However, the existence of Cu²⁺ species would decrease glycerol conversion and LA selectivity.

One of the recent studies, which reported promising results was the use of flower-like Bi₅W₁₆O₆₃ as a highly selective-visible-light photo-catalyst toward aerobic selective oxidation of glycerol to DHA using oxygen as oxidant in water at room temperature and atmospheric pressure [142]. Consequently, the highest DHA yield of 87% and selectivity of 91% were achieved by Bi₅W₁₆O₆₃ (B) sample at 96% glycerol conversion in 5 h. Fig. 7 demonstrates the proposed photo-catalytic reaction mechanism over Bi₅W₁₆O₆₃ (B) catalyst. Under visible-light irradiation, electron-hole pairs are generated by the semiconductor Bi₅W₁₆O₆₃ in water. The adsorbed glycerol on the surface of Bi₅W₁₆O₆₃ was oxidized by the positive holes to form the corresponding intermediate, which further reacted with oxygen and activated oxygen (e.g. O₂⁻) to produce the target product DHA. In addition, the adsorption capacity of DHA was weaker than glycerol over Bi₅W₁₆O₆₃, suggesting DHA can be easily desorbed from the surface of Bi₅W₁₆O₆₃, which was beneficial for obtaining high selectivity to DHA. Indeed, the photo-activity test on DHA in water over Bi₅W₁₆O₆₃ under visible-light irradiation suggested
that DHA was rather stable in the present photocatalytic reaction system, which could also be one of the reasons contributing to high DHA selectivity.

2.1.3. Multi-metallic based catalysts

Current research efforts have been primarily focused in two directions: (1) designing well-defined bimetallic noble metal catalysts and (2) incorporating earth-abundant metals to noble metal systems [143]. The high costs of noble metal catalysts and limited availability often pose significant economic challenges in practical applications of these catalysts. Replacing expensive noble metals with cost-effective non-noble metal catalysts without loss of performance will clearly make the aqueous phase oxidation (APO) of biomass economically sounds more attractive. Non-noble metals are believed to be able to tune the binding strength between functional groups and noble metals [74, 144]. Therefore, research efforts have been made to incorporate trace amounts of non-noble metal promoters such as Bi, Cu, Ni to noble metal systems [145]. These noble/non-noble metal combinations are found to effectively enhance Au, Pt, and Pd catalyst activity and selectivity, by preventing C–C cleavage of glycerol molecules [146].

The synthetic hydrotricalite-like solids, also called as layered double hydroxides (LDHs) generally qualify as clay [147]. However, when compared with cationic clay minerals, LDHs have wider range of chemical compositions of layers based on a different choice of metals in the framework and interlayer anions. The ratio of metal atoms within the layers can be finely tuned in a wide range. The calcination of LDHs also yielded metal oxide structures with well-dispersed active species [148]. The doping of additional transition metals into MgAl-based LDHs can further tailor the catalytic performance in the oxidation.

In fact, LDHs high melting temperature (2135 °C) and thermal stability combined with all other characteristics makes it to be a promising catalyst support for applications such as environmental catalysis and fine chemical production [149, 150]. For catalytic purposes, high surface areas are often desirable. Fortunately, over the last few years, LDHs have been successfully prepared by different methods, allowing one to obtain materials with tunable surface areas and chemical compositions.

For the first time, Zhou et al. [146] explored the possibility for an activation of molecular oxygen using a series of synthetic LDHs with hydrotricalite (HT)-like layered structures with the incorporation of a third metal (Ni, Zn, Cu, Co) as catalysts for the selective oxidation of glycerol. Cu/Al-Mg LDH catalyst showed the highest activity among all the tested samples at various conditions. FA was obtained as a main product with 51.27% selectivity at 86% glycerol conversion. However, the calcination of Cu–Al–Mg LDH sample at 650 °C for 6 h totally transformed the catalyst activity and product distribution. As a result, it reached to just 70.0% selectivity of FA at 97.3% glycerol conversion. In a similar study, Wang et al. [151] also used a series of Mg-Al LDHs supported by different transition metals of chromium (Cr), Manganese (Mg), Iron (Fe), Cobalt (Ca), and Copper (Cu). The activity test showed that only LDH-[Cu(SO3-Sole)] sample reached the highest GLYCA selectivity of 86.1% at 82% glycerol conversion. The main reason for the high activity of Cu supported sample was because Cu species enhanced the oxidation ability of O2 to primary alcohol in glycerol by reacting readily with –CHO group in intermediate of GLYLD.

Wu et al. [152] evaluated the addition of two amino modifiers in synthesizing a series of CuNiAl/HT catalysts (CuNiAl-HT-C6H5NH2 and CuNiAl-HT-C3H6NH2) for selective oxidation of glycerol to GLYCA. The CuNiAl-HT-C6H5NH2 sample with the highest basicity reached the highest GLYCA selectivity of 76% and 68.1% glycerol conversion at 60 °C in 4 h. The latter catalytic activity was similar to the mono-metallc Au/C commercial sample. This proves that the addition of amino groups led to the improvement in surface Lewis basicity of catalyst which enhanced the catalytic activity by the activation of the C–H bond of alkylo intermediate to form GLYLD. Similarly, the surface hydrophobicity of catalyst which led to the increase in GLYCA selectivity was enhanced by addition of amine groups.

Jin et al. [143] investigated two types of MgO–Al2O3 preparation methods namely co-precipitation (c) and modified sol-gel (s) on the activity of cobalt-based catalysts (Co0.15/MgAl2O4 and Co0.15/MgAl-s) in glycerol oxidation to di-carboxylic acids (TARA and OXALA). Co0.15/MgAl-c catalyst, prepared by co-precipitation method, indicated a relatively uniform distribution of Co, Mg, and Al elements on the catalyst surface. Authors believed that Co2+ species replaced the surface –OH groups of Mg3Al(OH)3(CO3)2 structure and formed surface M–O–@Co–O–M (M: Mg or Al) framework during modification. Consequently, Co0.15/MgAl-s catalyst reached about 90% product selectivity (64.4% TARA and 24.4% OXALA) at 100% glycerol conversion under mild conditions of 0.1 MP O2, at 70 °C and in 24 h.

After a few attempts in application of LDHs supported by various transition metals in oxidation of glycerol to GLYCA, Vijaya [149] synthesized Au NPs supported on three spinel-type MgAl2O4 (Commercial MgAl2O4, co-precipitation MgAl2O4, and flame pyrolysis MgAl2O4) support using three different techniques, which are tetrakis (hydroxymethyl) phosphonate chloride (THPD)-protected sol, deposition-precipitation with urea (DP calcined), and magnetron sputtering (MS). The characterization results revealed that all the samples uniformly coated with Au NPs except the THPC one, which indicated large areas of support material with no Au NPs coverage. The activity tests confirmed that all the tested samples exhibited typical trends of higher activity for smaller particle size. The DP-prepared catalyst on co-precipitated MgAl2O4 with the smallest particle size of 2.2 nm was found as the most active catalyst (1390 (Au mol)−1 h−1). In fact, this catalyst reached to more than 80% glycerol conversion with almost 50% GLY selectivity in 40 min. In addition, the co-precipitated THPC and FP-THPC samples with a quite similar particle size of 3.9 and 4.2 nm and different Al/Mg ratios of 6 and 4.2, respectively reached different products (Cu) selectivity (GLY and TAR). Surprisingly, the Au/Mg ratio was the main determining factor due to Al-rich surface promoting the C–C bond cleavage. Besides that, Au particle size also has been reported to have a high influence on product selectivity.

2.1.4. Non-metallic based catalysts

The recently developed “self-supporting” strategy [153] constitutes an attractive approach for immobilization of homogeneous catalysts. Different from the conventional approaches using various solid supports for homogeneous catalyst immobilization, the self-supported catalysts were constructed via supra-molecular assembly of a multi-topic bridging ligand with an appropriate metal salt. A coordination polymer is generated, with catalytic active sites that preserve the structural features of its homogeneous catalyst counterpart, but is insoluble in common solvents and thus obviates the need for an external support.
support [154,155].

Following the recent interest in exploring the applications of novel transition metal complexes in catalysis, supra-molecular chemistry, and material sciences [156,157] the preparation of main-chain iridium coordination polymers from rigid bis-benzimidazolium salt precursors and their application as self-supported catalysts in the oxidative conversion of glycerol to LA is carried out. Sun et al. [153] prepared a series of very interesting catalysis of NHC-Ir coordination polymers. The results of this study attracted much attention due to extremely high activity and selectivity of the prepared samples at mild reaction conditions. Also, the NHC-Ir sample exhibited an amazing reusability with up to 31 times just by a simple filtration process. The highest potassium lactate yield of 98% was obtained over NHC-Ir sample in air with glycerol (1.1 mL) catalyst volume 2.3 mg, KOH (2.5 mg), and H2O (8.3 mL) at 115 °C in 24 h.

One of the environmentally friendly alternative routes for glycerol oxidation is dehydrogenation via a hydrogen transfer reaction. In the last few decades, transfer hydrogenation has been developed as an efficient reduction method for organic substrates such as ketones, aldehydes and imines. These reactions are homogeneously catalyzed by transition metal derivatives, with the hydrogen donors generally employed being FA and 2-propanol. However, glycerol can be envisaged as a di-substituted 2-propanol, to perform a transfer dehydrogenation of glycerol in the presence of a suitable catalyst and an appropriate hydrogen acceptor. In principle, both primary and secondary hydroxyl groups of glycerol can be dehydrogenated, while, according to the relative oxidation potentials of secondary vs. primary alcohols, the hydrogen transfer is expected to selectively occur from the secondary hydroxyl group, yielding DHA as the main product. Table 3 illustrates a series of very interesting catalysis of NHC-Ir coordination polymers. The Au/Mg-Al catalyst with the strongest acidity (without Mg) reached the highest DHA selectivity (81.7%) and just 4.4% selectivity to GLYCA. Meanwhile, increasing the basicity to the highest amount (Mg/Al = 4.8) gave 49% and just 10.9% GLCYA and DHA selectivity, respectively.

2.2. Glycerol oxidation in base-free environment

As reported in previous sections, changing reaction conditions, support, and even structure of base material could significantly changed the catalyst activity and selectivity to the desired product. However, the conventional glycerol oxidation reaction in alkaline environment led to the formation of salts of the acids instead of free carboxylic acids which is desirable in industrial products. Thus, researchers are considering a base-free environment for oxidation of glycerol. The preliminary investigations revealed that the supported Pt catalysts are effective in this field. However, the catalysts enhance the C=C band cleavage and produce CO2 and FA, while leaching of Pt deactivated sample fast [18]. Various research groups are working intensely in search of various support materials, conditions, and metals for improvement of glycerol oxidation reaction to the desired products in a base-free environment. Thus, we report recent attempts on base-free glycerol oxidation reaction in the following section.

2.2.1. Mono-metallic supported catalysts

2.2.1.1. Au-based catalysts. As mentioned in Section 2.2, among noble metals, Pt is the most common metal that has been used in glycerol oxidation in base-free environment. Hence, applications of Au supported samples are rarely reported in this field. The study conducted by Liu et al. [161] investigated the glycerol oxidation to DHA in a base-free medium using different synthesized Au/Al2O3, Au/TiO2, Au/ZrO2, Au/NiO, and Au/CuO catalysts. The effects of various reaction temperatures, pressures, and catalyst loading evaluated to determine the optimal reaction conditions. The 2 wt%Au/CuO catalyst exhibited the highest activity among the synthesized sample with DHA yields up to 80% at 40–50 °C. In fact, for the first time, this study obtained DHA as the only primary product of glycerol oxidation reaction using supported Au NPs in the base-free conditions.

Yuan et al. [162] investigated the effect of acid-base property of the Au/Mg-Al catalyst on the catalytic activity. The variation in Mg/Al ratio of support led to significant changes in catalysts textural characteristics. Increasing the Mg/Al ratio from 0 to 4.8 reduced the surface area from 222 to 197 m2/g, while the pore volume and pore diameter increased from 0.28 to 0.71 cm3/g and 3.6 to 11.7 nm, respectively. Various Mg/Al ratios also led to the significant changes in product distribution of glycerol oxidation. The Au/Mg-Al catalyst with the strongest acidity (without Mg) reached the highest DHA selectivity (81.7%) and just 4.4% selectivity to GLYCA. Meanwhile, increasing the basicity to the highest amount (Mg/Al = 4.8) gave 49% and just 10.9% GLCYA and DHA selectivity, respectively.

2.2.1.2. Pt-based catalysts. One of the earlier attempts which confirms successful glycerol oxidation to a desired product (e.g. GLCYA) in the base-free condition performed by Mengyuan et al. [163]. They evaluated the application of different AC size (253.2–9.3 μm) as support for Pt mono-metallic catalyst. Initial findings revealed that Pt NPs were highly dispersed on support surface with average particle size of 2.8–5 nm. The SS5 (5 wt% Pt supported on activated carbon which was ball milled for 50 min) sample reached to 46.7% yield of GLCYA at 70.3% glycerol conversion at 60 °C in 6 h. In fact, the Pt/C catalyst activity increased from 50 to 70.3% by decreasing the AC support particle size from 253.3 to 9.3 μm. The main reason for the latter surge of catalytic activity was higher accessibility of reaction to the Pt NPs. Three types of Pt supported carbon nano-fibers (CNF) catalyst (Pt/CNFs, Pt/S-CNFs, and Pt/HNO3-CNFs) were synthesized by Zhang et al. [164]. The Pt/S-CNFs sample possessed the smallest Pt particle size (1.5–1.8 nm) among the three prepared catalysts. It conferred the highest-glycerol conversion (89.9%), almost two times higher than glycerol conversion over Pt/CNFs (30.1%) and Pt/HNO3-CNFs (47.3%) with 83.2% selectivity to GLYCA in 6 h reaction time at 60 °C. In addition, Wang et al. [165] synthesized a series of Pt supported on mesoporous carbon nitride (MCN) samples. The Pt particle size decreased from 3.4 nm to 2 nm in Pt/MCN-1 to Pt/MCN-6, respectively by increasing the N content in the support. However, the surface area (S BET), pore volume (Vp), and pore diameter (Dp) increased significantly. The activity test exhibited that the support basicity enhanced the glycerol oxide, GLYLD and GLYCA. In particular, 58.3% GLYCA and 24.3% GLYLD yields at 63.1% glycerol conversion were obtained at 60 °C in 4 h over the Pt/MCN-5 sample. The Pt/MCN-6 sample with the smallest

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Oxidants</th>
<th>Other reaction conditions</th>
<th>Y (%)</th>
<th>Sol (%) or Y (%)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir (1,5- hexadiene) (4,7-dimethyl- 1,10- phenanthroline) Cl</td>
<td>Acetophenone</td>
<td>A Schlenk tube; 373 K; 0.5 h; [Ir] = 3.0 × 10−3 M; [R₁CO₂]/[Ir] = 2</td>
<td>78</td>
<td>47 (S Pt)</td>
<td>[158]</td>
</tr>
<tr>
<td>[Ir(cod)P₂N(CH₂CH₂PPh₂)₂]</td>
<td>Benzaldehyde</td>
<td>5.0 mmol H₂O₂ (35% in H₂O)</td>
<td></td>
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<tr>
<td>[O C C₆H₄(N(CH₂CH₂O)₃)₃] (BOH)₄(BF₄)₂</td>
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</table>
Pt particle size reached the lowest GLYCA selectivity with higher C1 products selectivity.

Initial studies on application of CNTs as a support for catalytic oxidation of glycerol in a base free environment were reported about a decade ago. Generally, there are limited numbers of studies on the application of CNTs in base-free condition. Zhang et al. [164] had confirmed that N-doped MWCNT could enhance the dispersion of Pt on support and reduced the Pt particle size to 1.8 nm. Indeed, the Pt/N-MWCNT-973 could reach 83% GLYCA selectivity at 54.9% glycerol conversion; almost double the glycerol conversion over the Pt/MWCNT at 60 °C. Lei et al., [88], for the first time, evaluated the effect of metal particle size on catalytic activity in the base-free environment. Indeed, increasing Pt loading from 2 to 8 wt% increased the Pt NPs size from 1.5 to 2.9 nm in the Pt NPs/CNT samples. The catalytic activity reached its peak (TOF = 1000 h⁻¹) for Pt size up to 2.5 nm. In addition, larger Pt NPs size also enhanced GLYLD selectivity (8 wt% Pt/CNTs – 43.5%), while smaller size Pt NPs (2 wt% Pt/CNTs) favors GLYLD transformation to GLYCA by 54% selectivity. Indeed, smaller Pt NPs with more atoms at vertices and edges, strongly adsorb hydroxide, and favored the formation of terminal diol.

Ricahrd et al. [166] reported interesting findings on application of polymer-supported Pt catalyst (Pt/PDVB-dep, Pt/SPDVB-dep, Pt/PDVB-imp, Pt/SPDVB-imp) in glycerol oxidation reaction in a base-free condition. In this study, the activity of the polymer supported catalysts was compared with the commercial Pt/C and Pt/Al₂O₃ samples. Pt NPs were deposited in defined size, content, and distribution on the polymer. All of the prepared samples have similar Pt size of 1.5–6 nm. The activity test revealed that polymer supported samples were as active or even more active than carbon catalyst with almost 95% glycerol conversion compared to 90%. These samples also exhibited 60% GLYCA selectivity compared to 40% over Pt/C sample during a 24 h reaction time at 60 °C. Furthermore, the polymer supported sample product yield was twice more (60%) than Pt/Al₂O₃ with just 30% GLYCA yield in the first 8 h of reaction. In fact, polymers could change the polarity of the support from hydrophobic, which is a major factor influencing catalytic performance, to the hydrophilic. The results of this study affirmed that polymeric support is highly potential to be used as a support in glycerol oxidation reaction instead of commercial oxides and carbons.

2.2.2. Bi-metallic based catalysts

Ning et al. [167] was the first group to demonstrate soluble Bi species in reaction solution could enhance the catalytic performance of Pt/NCNT catalyst for selective oxidation of glycerol to DHA in a base-free environment. Initially, they used Pt/NCNT as catalysts with an average diameter of 3.2 nm. It reached 60.5% selectivity of GLYCA at 31.5% glycerol conversion and 11% DHA selectivity. Then pre-loaded Bi sample (Pt-Biₓ/NCNT) significantly increased the DHA selectivity to 55.5%. The initial reaction rate also improved from 66.2 mmol/m²h for Pt/NCNT to 107.4 (mmol/m²h) for Pt-Biₓ/NCNT sample. Furthermore, concurrent application of 100 mg Pt/NCNT and 50 mg Bi/NCNT increased the DHA selectivity to 53.5% at 34.3% glycerol conversion, which was almost similar to Pt-Biₓ/NCNT activity. The experimental studies demonstrated Bi leaching from Bi/NCNT and Bi adsorption on Pt/NCNT performance. If similar performance can be achieved by using a simple mechanism mixture, the preparation of catalyst might be simplified. Thus, a direct application of Bi salts or oxides into the reaction solution was performed in order to confirm the hypothesis. The addition of Bi(NO₃)₃·5H₂O, BiCl₃ and Bi₂O₃ to the reaction medium led to a significant improvement of DHA selectivity from 11.1% to 64.1%, 57.5%, and 59.2%, respectively. Thus, regardless of the way how Bi was introduced to the reaction system, similar enhancement of DHA selectivities could be reached. The optimal amount of Bi(NO₃)₃·5H₂O was about 1 wt% for achieving 78% DHA selectivity. The Biₓ/NCNT (in-situ) system exhibited 10% higher conversion compared to Pt-Biₓ/NCNT sample. Further investigation with antimony (Sb) instead of Bi also confirmed the earlier findings in this study and DHA selectivity increased to 80.5% using Sbₓ-Pt/NCNT (in-situ) system. Therefore, the researchers concluded that the promotion mechanism might be universal across the group 5 metals.

Fig. 8 illustrates the mechanism of Biₓ-Pt/NCNT (in-situ) system for selective oxidation of glycerol to DHA. Pt/NCNT sample is active and selective for the production of GLYLD from glycerol (Fig. 8a). However, Bi₃⁺ was adsorbed onto Pt NPs to firstly occupy the high-energy step sites, and then the terrace sites, in the presence of soluble Bi₃⁺⁺ in the reaction solution. As a consequence, the selectivity was tuned by blocking the high-energy Pt sites where the adsorption and activation of primary hydroxyl groups or over-oxidation and transformation of DHA were preferred. Finally, the Bi-Pt sites were formed on the terrace surfaces of Pt NPs through the geometrical blocking effect (Fig. 8b). The DHA selectivity improved on these sites due to the chelation effect of Bi-Pt catalysts with the secondary hydroxyl group of glycerol.

Brett et al. [168] evaluated the application of two bimetallic catalysts in oxidation of glycerol to C3 products (GLYLA and TARA) at ambient temperature (23 °C). The Au-Pt/MgO and Au-Pd/MgO were synthesized by immobilizing colloidal metal particles on MgO support. The initial experimental results revealed that the metal molar ratios and support material had strong effect on the catalytic activity. The Au-Pt/MgO catalyst with 1:1 mol fraction reached about 80% selectivity of C3 products at 60 °C. However, the selectivity of C3 products obtained was about 90% at just 40 °C by increasing the metal ratio of Au/Pt (1/3). The catalyst still exhibited high conversion (42.5%) with more than 88% selectivity of C3 products when extending the reaction time to 24 h and simultaneously decreased the reaction temperature to just 23 °C. All the experimental runs on the Au-Pt/MgO catalyst indicated that it was more active and selective to C3 products compared to the Au-Pd/MgO sample. In addition, Shen et al. [169] reported synthesizing the Au-Pt/TiO₂ with Au/Pt atomic ratio of 3/1, which exhibited high activity with 50%, 30%, and 20% selectivities to GLYLD, DHA, and GLYCA. The Au-Pt/TiO₂ catalyst with higher Pt content actually led to higher selectivity to GLYLD and GLYCA while with higher Au content the DHA formation was enhanced. These effects indicated the role of electronic properties of the catalyst in tuning, not only activity but also selectivity to desired products in the glycerol oxidation.

Villa et al. [170] conducted a study on the application of supported Au catalysts for oxidation of glycerol in acidic environment. A series of monometallic clusters deposited on AC, TiO₂, MgAl₂O₄, and H-mordenite zeolite were synthesized by sol immobilization technique. Initial findings exhibited that 1%Au/AC, 1%Pd/AC, and 1%Pt/AC samples achieved very low catalyst activity with C1 molecules (e.g. FA) as the main product. Meanwhile, 1%Au/H-mordenite and 1%Pt/H-mordenite samples indicated C1 products reduced, but C3 products increased significantly. Thus, they concluded that the support material was crucial in products selectivity. Furthermore, they continued their study and prepared a range of supported bimetallic Au-Pt catalysts by sol immobilization method using acidic (H-mordenite, SiO₂, MCM-41), and sulfated ZrO₂ and basic (NiO and MgO) oxides as supports [171]. In terms of activity, the presence of a basic support such as MgO (isoelectric point of 10.4) increased the activity (657 mol molAuPt⁻¹ h⁻¹) superior to those observed when the same Au-Pt NPs were immobilized on NiO (283 mol of glycerol molAuPt⁻¹ h⁻¹) and the acidic supports (113, 105, and 228 mol of glycerol molAuPt⁻¹ h⁻¹ for S-ZrO₂, H-mordenite, SiO₂ and MCM-41, respectively). Indeed, a higher selectivity to C3 compounds (GLYCA + GLYLD + TARA + DHA) (~95%) was obtained using acidic supports whereas basic supports, in particular MgO, promoted C=C bond cleavage, forming C2 and C1 products in high amounts (59%).

Hirasawa et al. [172] studied the performance and reaction mechanism over a bimetallic Pd-Ag/C catalyst in selective oxidation of
glycerol to DHA. Initially, the performance of various Pd/C samples with Ti, Mn, Ni, Re, Ir, Au, and Bi was compared with Pd-Ag/C catalyst and the highest DHA selectivity of 81.9% was achieved over Pd-Ag/C sample. In addition, application of various supports was tested (SiO2, TiO2, Al2O3, ZrO2, and CeO2) for Pd-Ag catalyst. All the supports except CeO2 reached more than 80% DHA selectivity. However, the glycerol conversion reported was less than 20% for all the tested samples. The addition of Ag to Pd improved the interaction between glycerol and the catalyst surface. The adsorption of carboxylic acids with β-hydroxyl group, 1,3-dicarboxylic acids, and the ketones with β-dicarbonyl structure on Pd blocked the sites for oxygen activation causing the deactivation of the Pd-Ag/C sample.

2.2.3. Non-metallic based catalysts

In the study conducted by Sharninghausen et al. [173], a series of iridium (Ir) complexes samples were synthesized as the first homogeneous catalysts for the conversion of glycerol to LA in the base-free environment. These samples had higher activity and selectivity than the previously reported heterogeneous systems. In addition, H2 was generated as a useful by-product. The advantage of their method fulfills the main principles of green chemistry since the process required mild conditions, solvent free, renewable feedstock, degradable product and catalyst loadings as low as 0.003 mol%. The highest LA selectivity of 96.6% was achieved at 94% glycerol conversion over the spectacular C12H16IrN4O2.BF4 catalyst with 15:1 ratio of glycerol/water after 24 h. The synthesized iridium sample gave selectivities higher than previously reported heterogeneous systems. In detail, the first step was Ir-catalyzed dehydrogenation of glycerol to GLYLD or GLYLD, which then can be converted into LA (in the form of lactate) under alkaline conditions. However, the synthesized iridium sample gave selectivities higher than 95% for LA-the highest as reported to date for any chemo-catalyzed processes and more typical of fermentative processes. The by-product H2 could also be employed elsewhere in a commercial plant reducing the overall cost of the process. Fig. 9 depicts reaction pathways of glycerol to LA or GLYLD, which are known to interconvert in alkaline media. Based on the literature, authors believed that the Ir precursors synthesized in this study might be more selective for the dehydrogenation of the secondary alcohol to yield DHA over GLYLD, consistent with our observation that DHA led to higher yields of LA than GLYLD when used as starting material. Subsequent base-catalyzed dehydrogenation of GLYLD would lead to PAL and its enol form, which reacts by an intra-molecular Cannizzaro reaction to yield LA. The major side product observed was EG, which is probably produced from GLYLD by a retro-aldol reaction, with concomitant formation of FA.

Despite the enormous applications of zeolite and heteropoly acid (HPA) catalysts as active components in various heterogeneous catalytic processes, application of these types of catalysts are rarely reported in glycerol oxidation reaction. For the first time, application of zeolite in a continuous oxidation reaction investigated by Lari et al. [174] using iron containing zeolite catalyst in the presence of molecular oxygen. They synthesized a series of iron containing catalysts (FeA, NaFeA, Fe-Z-s873, Fe-Z-s1173, Fe5, Fe-S-s873, Fe5A-s1173, Fe2Z4O, Fe/Z1000, and Fe/S) using different preparation methods of various catalysts with different Bronsted or Lewis acidic site concentrations and strengths. However, among the prepared samples, the Fe-S-s873 catalyst which prepared by isomorphous substitution of iron in the all-silica framework followed by activation by steam (873 K) reached DHA yield of 90% due to its mild activity and high dispersion of iron species in the form of isolated cations or small FeOx clusters in extra framework positions.

2.3. Bio-catalysis

Glycerol can also be oxidized with biocatalysts, such as enzymes and microorganisms to produce DHA [28]. Initially, Bertrand observed the production of DHA from glycerol through a bacterial route in 1898. The Sorbose bacillus was used to oxidize certain secondary alcohols to their corresponding ketone. The Sorbose bacillus was found to be identical with the acetic acid bacterium Bacillus xylitum. DHA was produced from the enzymatic activity of DHA-lyase (DHAL) in carboxydebaeterium, Acinetobacter sp. strains jcl Dsm3803, when it was grown in methanol [175]. Intact cells of the following microorganisms, Acetobacter suboxydans ATCC 621, Acetobacter xylitum a-9, Glicobacter melanogenus IFO 3293, and G. melanogenus IFO3294, were studied for their glycerol oxidizing activity [176]. As a result, the
promote electron transfer from the substrate to the enzyme [186]. In the substrate range, the use of mediators has been recommended to improve H2O production. During the oxidation process, the mediator reduces oxidized electron shuttles. Mediators act as catalysts by reducing the activation energy of the reaction [187]. Liebminger et al. [186] used 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at low concentrations (< 6 mM) to promote the conversion of glycerol in the presence of laccase from Trametes hirsuta to GLYLD. Higher concentrations increased the conversion rate of glycerol but decreased the selectivity, and compounds like GLYCA and TARA are formed. The pH of the medium played an important role because TEMPO decomposed and the enzyme was inactivated under acid conditions (pH 4). A patent by Wolf [188] reported the production of GLYLD via the reaction of glycerol with a methanol dehydrogenase purified from Methylobacterium organophilum. The culture medium for the bioconversion contained up to 20% glycerol with pH in the range of 5–11, and the temperature ranging from 5 to 50 °C under aerobic conditions. Maximum conversion of 35% of the glycerol was reported in a period of 24 h. The enzymatic production of GLYCA from glycerol has also been achieved through oxidative fermentation by the action of acetic acid bacteria such as Acetobacter and Gluconobacter strains in a jar fermenter. A bioconversion of 136.5 g L⁻¹ was obtained when using G. frateurii and 101.8 g L⁻¹ with A. Fropicallis [189].

As the glycerol molecule is a small uncharged molecule, it can cross the inner cell membrane through an integral membrane protein (glycerol uptake facilitator, GlpF, in the case of Escherichia coli) which enables facilitated diffusion. Glycerol can be metabolized to glycerol-3-phosphate via glycerol kinase (GlpK) for glycerol uptake and metabolism. A nanoparticle-supported enzyme system was described [185] for the bio-transformation of glycerol into DHA (yield of 160 g per g immobilized enzyme) using glycerol dehydrogenase from Cellulomonas sp. This has revealed the possibility of producing value-added chemicals from bio-renewable resources with in-situ co-factor regeneration through designed reaction pathways from not native to living organisms. When the redox potential of the microorganism is a limitation for the substrate range, the use of mediators has been recommended to promote electron transfer from the substrate to the enzyme [186]. During the oxidation process, the mediator reduces oxidized electron shuttles. Mediators act as catalysts by reducing the activation energy of the reaction [187]. Liebminger et al. [186] used 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at low concentrations (< 6 mM) to promote the conversion of glycerol in the presence of laccase from Trametes hirsuta to GLYLD. Higher concentrations increased the conversion rate of glycerol but decreased the selectivity, and compounds like GLYCA and TARA are formed. The pH of the medium played an important role because TEMPO decomposed and the enzyme was inactivated under acid conditions (pH 4). A patent by Wolf [188] reported the production of GLYLD via the reaction of glycerol with a methanol dehydrogenase purified from Methylobacterium organophilum. The culture medium for the bioconversion contained up to 20% glycerol with pH in the range of 5–11, and the temperature ranging from 5 to 50 °C under aerobic conditions. Maximum conversion of 35% of the glycerol was reported in a period of 24 h. The enzymatic production of GLYCA from glycerol has also been achieved through oxidative fermentation by the action of acetic acid bacteria such as Acetobacter and Gluconobacter strains in a jar fermenter. A bioconversion of 136.5 g L⁻¹ was obtained when using G. frateurii and 101.8 g L⁻¹ with A. Fropicallis [189].

Fig. 9. Reaction pathways of glycerol to lactic acid (green) and other common by-products (red) [173].
minimized enzyme product inhibition and maximized thermal stability.

2.4. Summary

In summary, different types of supports (carbon supports, carbon nano-tubes (CNTs), Mg-Al layered-double hydroxides (LDHs), metal-oxides, and polymeric supports) with combination of various noble metals (e.g. Au, Pt, Pd) have been widely used in glycerol oxidation reaction to synthesize a novel catalyst with high stability and activity. The majority of research studies reported that the presence of particular noble metal or support as the most influential factor on catalyst activity. Besides, the number of basic sites, synthesize method, pore size, and application of bi- or tri-metals instead of mono-, have been reported as other influential factors to achieve higher activity of the synthesized catalysts.

In particular, application of sol-immobilization approach for catalytic synthesis exhibits significant effect on NPs pore and particle sizes and activity of the final sample. However, conventional synthesizing methods such as impregnation suffer from poisoning and rapid deactivation. In addition, photo-catalytic oxidation of glycerol is a very interesting approach for transformation of glycerol to value-added chemicals due to its environmentally friendly characteristics and moderate reaction parameters. Unfortunately, besides acceptable results that are obtained in this method, there are still limited numbers of studies in this area.

Also, it is recommended that application of noble metals should be restricted due to their non-economical nature as well as their limited availability in future. Application of other types of catalysts such as supported hierarchical zeolites, heteropoly acids, and even metal-organic frameworks (MOFs) in this field is rarely reported. These types of catalysts have showed acceptable results in other research areas and it is recommended the application should start or accelerate the glycerol oxidation process. In fact, application of in-effective synthesis approaches (e.g. impregnation) and materials (e.g. carbon and noble metals) should be replaced with novel ones to reach the ultimate goals, which are production of value-added chemicals through bio-refineries instead of petrochemical industry.

3. Electro-chemical oxidation of glycerol

The electro-chemical oxidation of glycerol has been a subject of growing interest among researchers in the last few years [208–210]. Glycerol oxidation to CO2 generates 14 F mol$^{-1}$, which is more than twice them ethanol energy content. Furthermore, glycerol is produced in large amounts as a by-product (10% w/w) in biodiesel manufacturing and can be considered as a potential candidate for fuel cells. In this context, the knowledge about the mechanism of electro-oxidation of glycerol must be improved before practical systems with appropriate catalysts can be designed. Concerning this issue, recent studies have provided important information about the electro-oxidation pathways by using high performance liquid chromatography [211] and in-situ FTIR spectroscopy [210,212,213].

The main advantage of the electro-chemical process when compared to other oxidation processes is better control of the desired products selectivity when the reaction is performed in aqueous media with low reaction temperature and pressure. The electro-chemical oxidation of glycerol can be performed in fuel cell and electrolysis cell through a reversed ionic diffusion migration process which is anion-exchange membrane (AEM) or a direct proton diffusion migration process also known as proton-exchange membrane (PEM). The fuel cell leads to co-generation of value-added chemicals and electrical energy through direct oxidation reaction of glycerol at the anode and reduction of oxygen at the cathode (Fig. 10a). However, the electrolysis cell leads to co-generation of hydrogen and value-added chemicals as well as water reduction at the anode and cathode, respectively (Fig. 10b). In a PEM, instead of just water, the anodic side contains an aqueous solution of the organic compound. The organic compound and water are oxidised to CO2, H+ and electrons at the anode. The H+ travels through the membrane where it recombines with the electrons, which have passed through the external circuit to form pure H2 gas at the cathode. The external circuit provides the electrical potential to drive the reaction (Fig. 10c). In an AEM, the fuel is supplied at the anode and oxygen through air, and water are supplied at cathode. Fuel is oxidized at anode and oxygen is reduced at cathode. At cathode, oxygen reduction produces hydroxides ions (OH$^-$) that migrate through the electrolyte towards the anode. At anode, hydroxide ions react with the fuel to produce water and electrons. Electrons go through the circuit producing current (Fig. 10d). The overall electro-chemical oxidation of glycerol into hydrogen presented in Eq. (5):

$$\text{C}_3\text{H}_6\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{O}_2 + 7\text{H}_2$$  \hspace{1cm} (5)

with the anode and cathode reactions given by Eqs. (6) and (7):

$$\text{C}_3\text{H}_6\text{O}_3 + 3\text{H}_2\text{O} \leftrightarrow \text{C}_3\text{O}_2 + 14\text{H}^+ + 14\text{e}^-$$  \hspace{1cm} (6)

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Products obtained</th>
<th>Yield</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clostridium pasteurianum</td>
<td>Butanol, 1,3-propanediol</td>
<td>17 g L$^{-1}$, 30 mol%</td>
<td>[192][193]</td>
</tr>
<tr>
<td>Klebsiella pneumoniae</td>
<td>Ethanol, Lactate</td>
<td>18 mol% under phosphate limitation and 34 mol% under iron limitation</td>
<td>[194][195]</td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>Ethanol, Succinic acid</td>
<td>35–45 g L$^{-1}$, 5.5 g L$^{-1}$ h</td>
<td>[196]</td>
</tr>
<tr>
<td>Clostridium Butyricum</td>
<td>Ethanol, Propionic acid</td>
<td>35–45 g L$^{-1}$, 5.5 g L$^{-1}$ h</td>
<td>[197]</td>
</tr>
<tr>
<td>Clostridium Freemanii</td>
<td>Ethanol, Lactic acid</td>
<td>25 g L$^{-1}$, 4.6 g L$^{-1}$</td>
<td>[198]</td>
</tr>
<tr>
<td>Clostridium Plantisola</td>
<td>Ethanol, Formate</td>
<td>30 mmol L$^{-1}$, 32 mmol L$^{-1}$</td>
<td>[199]</td>
</tr>
<tr>
<td>Schizochytrium Limacinum</td>
<td>DOOHxanoenoic acid</td>
<td>Yield: 1.68 g L$^{-1}$, productivity: 0.28 g L$^{-1}$ day</td>
<td>[200]</td>
</tr>
<tr>
<td>Enterobacter aerogenes</td>
<td>Ethanol, Hydrogen</td>
<td>0.96 g L$^{-1}$ at 0.85 mol mol glycerol$^{-1}$</td>
<td>[201]</td>
</tr>
<tr>
<td>Propionibacterium freudenreichii sp. shermanii</td>
<td>Vitamin B12</td>
<td>0.81 mg mL$^{-1}$ in batch culture</td>
<td>[202]</td>
</tr>
<tr>
<td>Propionibacterium acidopropioni</td>
<td>Propionic acid</td>
<td>4.62 $^{-1}$, 12 g L$^{-1}$ and 0.20 ± 0.0075 g L$^{-1}$ h</td>
<td>[203][204]</td>
</tr>
<tr>
<td>Anaerobic lipopolis sucinicicproducens</td>
<td>Succinic acid</td>
<td>106 g L$^{-1}$</td>
<td>[205]</td>
</tr>
<tr>
<td>Glaucobacter Rossydu</td>
<td>Dihydroxyacetone</td>
<td>385 g in 34 h from 400 g glycerol</td>
<td>[206][207]</td>
</tr>
<tr>
<td>Aceto bacter tropicalis</td>
<td>D-glyceric acid</td>
<td>22.7 g L$^{-1}$ from 200 g L$^{-1}$ glycerol in 4 days</td>
<td>[188]</td>
</tr>
</tbody>
</table>
In order to produce hydrogen by electrochemical reforming at a viable rate it is necessary to have fast reaction kinetics. However, the glycerol oxidation reaction is complex, thus it is predicted there may be a large over-potential required in order for the reaction to proceed at a reasonable rate. Therefore, choosing a suitable electro-catalyst to minimize this over-potential will be critical. Based on the types of products which can be obtained in a PEM reactor, there are three main reaction pathways: partial oxidation, dissociative oxidation, and dehydration.

Fig. 11 exhibits a summary of possible reaction pathways occurring in this system. First, glycerol is oxidized to GLYLD, isomerized to LA, and further oxidized to GLYCA [214]. GLA and CO₂ are formed by C–C

\[
14H^+ + 14e^- \rightarrow 7H_2
\]  

(7)

Fig. 10. Working principle of (a) fuel cell, (b) electrolysis cell, (c) proton exchange membrane (PEM), and (d) anion exchange membrane (AEM) [29].

Fig. 11. Glycerol oxidation pathways in a PEM reactor [214].
bond cleavage. The third pathway is the formation of acetol, which can be produced via acid-catalyzed dehydration in contact with a Nafion® membrane. Nafion® can be the source for the protons for this reaction as it is highly acidic when hydrated.

The first report related to the successful co-generation of chemicals and energy by electro-chemical oxidation of glycerol was accounted by Simoes et al. [29] in 2012, followed by Zhong et al. [215] who evaluated electro-catalytic oxidation of glycerol for co-generation of value-added chemicals and electricity over a Pt/C anode catalyst in an anion exchange membrane fuel cell. The results revealed that the pH of the reaction media, glycerol concentration, and electrode over potential had significant impact on the desired products (C3 acids) selectivities.

The first successful attempt for electro-catalytic oxidation of glycerol to only value-added chemicals was reported by Ciriminna et al. [216]. In their work, OXALA with 98% selectivity at 100% reaction conversion in the selective oxidation of glycerol using a Br/TEMPO catalyst was reported. They used 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) in the presence of NaOCl as a regenerant oxidant at pH 10 and 275 K. They observed amount of DHA and TARA increased as intermediate by-products in the presence of micro-porous sol-gel silica glasses dopped with TEMPO. To explain the improvement of catalytic activity, it should be considered that in contrast to traditional surface derivatisation methods that leave the anchored nitroxyl radicals unprotected at the material surface, the sol-gel homogeneous encapsulation isolates the radicals within nano-porous sol-gel cages, that is within the hundreds of square meters per gram of internal surface area (430 m²/g for 5G-TEMPO) compared to the negligible amount of molecules entrapped at the outer reaches (1 ± 2 m²/g) of the particulate material. And it is precisely this unique structural feature of sol-gels that protects the radicals from the intra-molecular quenching of the molecules bound in proximity at the silica surface, which was recently found to be responsible for the continuous decrease in the activity of silica-anchored TEMPO in consecutive alcohol oxidation runs with OCI/Br as internal oxidant.

Criminna et al. [217] obtained 25% yield of DHA during a waste-free glycerol electro-chemical oxidation reaction at the anode through the application of a small electron potential (1.1 V vs Ag/AgCl) to a glycerol/water solution (0.05 M) with bio-carbonate (0.2 M) at pH 9.1 using 15 mol% TEMPO after 20 h. The results revealed that long reaction time up to 200 h did not cause over-oxidation to carboxylic acid.

Even though there are limited numbers of research studies on electro-chemical oxidation of glycerol reported in literature [27,28], the knowledge related to the electro-catalytic oxidation of glycerol have expanded significantly during the last five years which reflected the importance of value-added chemicals such as DHA, GLYCA, MA, and TARA as bio-renewable source such as glycerol. Similar to the catalytic oxidation of glycerol, the elector-catalytic reaction could also be performed in both alkaline and base-free environments. However, the majority of electro-catalytic oxidation of glycerol studies has been performed in the alkaline environment but only few in acidic or neutral (base-free) environments.

The application of noble metals NPs such as Au, Pt as electrodes in acidic or alkaline media or supported metal NPs for electro-catalytic oxidation of glycerol in simultaneous generation of value-added chemicals and energy has attracted much attention recently [218,219]. Grace and Pandian [88] reported the first novel process of noble metals NPs (Pt, Pt-Pd, and Pt-Pd/Ru) dispersion in nanometer scale onto conducting polymer materials without using bulk Pt electrodes for glycerol oxidation. Pt-Ru supported poly-aniline sample registered the highest activity in glycerol oxidation reaction. Initial studies carried out in the presence of supported mono-metallic Pt/C and Pd/C samples. However, Pt is very expensive and Pt and Pd deactivation during electro-catalytic oxidation reaction in prolonged reaction time are major disadvantages of Pt and Pd noble metals [220]. Thus, application of Au NPs on various support materials was proposed as the most effective method for oxidation reaction. In addition, during the last few years some techniques have been developed for clearer or higher quality detection of products during the electro-catalytic reaction. For instance, the in-situ FTIR and isotopically labeled glycerol was proposed to study the C–C bond cleavages of glycerol and the 13CO2 and 12CO2 behaviors in the electro oxidation of glycerol over polycrystalline Pt [221]. The second method is [211] the combination of cyclic voltammetry (CV) and online chromatographic techniques for faster detection of products in glycerol oxidation reaction. These detection methods provided a detailed insight to the different mechanisms of glycerol oxidation on Pt and Au electrodes. Table 5 summarizes some of the previous studies in electro-catalytic oxidation of glycerol to value-added chemicals.

### Table 5

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction conditions</th>
<th>Con (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sel (%) or Y (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>1.0 M glycerol, 0.5 V fuel cell voltage, 6 h</td>
<td>20.4</td>
<td>83 [215]</td>
<td></td>
</tr>
<tr>
<td>Pt/C</td>
<td>150–500 mV electrode potential, 70–200 kJ/mol activation energy, 508–533 K</td>
<td>–</td>
<td>80 [218]</td>
<td></td>
</tr>
<tr>
<td>Pd₈O₅NiO₅/C</td>
<td>A three-electrode cell, onset potential of 0.4 V, 4 h</td>
<td>30</td>
<td>45 [219]</td>
<td></td>
</tr>
<tr>
<td>Pd₈O₅Ag₂O₅/C</td>
<td>&lt; 0.45 V potential, 12 h</td>
<td>24</td>
<td>[222]</td>
<td></td>
</tr>
<tr>
<td>Au/C-AQ</td>
<td>1.5 V onset potential, 50 °C, 6 h</td>
<td>95.6</td>
<td>61.8 [219]</td>
<td></td>
</tr>
<tr>
<td>Au/C-NC</td>
<td>82.2</td>
<td>95.5</td>
<td>[223]</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Conversion.  
<sup>b</sup> Selectivity or yield.

3.1. Mono-metallic supported catalysts

3.1.1. Au-based catalysts

Recent studies revolve on application of Au NPs with or without metal NPs supported on different types of carbons. Electro-oxidation of glycerol over a new series of Au NPs on various support catalysts (extended poly (4-vinylpyridine) functionalized graphene (Au-P4P/G), carbon black (Au-CB), P4P functionalized reduced graphene oxide (Au-PmAP/G), and poly (m-aminophenol) (Au-P4P/rGO)) revealed that Au-P4P/G possessed the highest activity toward C₂ products [224]. High activity of catalyst could be attributed to the weakest interaction between Au NPs and GLYCA. The lowest d-band center of Au-P4P/G facilitated desorption of GLYCA to desorbs from Au surface and hindered further decomposition of GLYCA into other products. The Au-P4P/G catalyst could achieve 68.6% GLYCA production at 0.2 V and the ratio between C₂ products and others (C₁ + C₂) was 4.92 compared to the Au-CB with just 0.96.

The main focus of some research is merely on improving the electro-oxidation reaction conditions and finding the optimum amount of parameters in this field to enhance the catalytic activity. The evaluation related to the effect of 1–20 wt% Au loading on the Au/C electrode activity indicated that high amount of Au loading inhibited formation of Au oxide reducing glycerol oxidation due to poisoning caused by
accumulation of glycerol oxidation products within the layers [225]. In another study, the effect of three different particle sizes (≤ 4.7 nm, 14.7 nm, and ≥ 43 nm) of Au/C catalyst was investigated. The catalyst with the smallest particle size unexpectedly registered the highest activity. The Au/C with particle size less than 4.7 nm had twice the activity of Au/C with particle size larger than 43 nm. Fundamentally, small Au particle could provide the main requirement of a fuel cell catalyst namely high mass activity, low over potentials and high stability [226]. de Souza et al. [227] further compared the application of different 3-carbon-atom chain alcohols with glycerol. 1-propanol, 2-propane-1,2-diol and propane-1,3-diol were used in the electro-oxidation process on Au electrode in an alkaline medium. The results indicated that the reactivity of alcohols decreased in the following order: glycerol > propane-1,2-1,2-diol > propane-1,3-diol > 2-propanol = 1-propanol. Interestingly, glycerol and propane-1,2-diol exhibited high C–C bond breaking rate due to the presence of products with C1 and C2 atom chain. However, the electro-oxidation of other alcohols led to products with C3 atom chain. Thus, the presence of vicinal OH groups in the alcohol molecule is a key component for the C–C bond cleavage in alkaline environment. In fact, more electrons per alcohol molecule and a higher current density could be produced. Finally, Zhang et al., [228] reported that the addition of CeO2 in Au/C catalyst significantly improve catalytic performance for glycerol electro-oxidation. More negative shift was obtained after addition of CeO2 to the Au/C sample compared to the Au/C catalyst. The peak current densities (jp) over Au-CeO2/C and Au/C samples were 75.4 and 20.4 mA cm−2 and the current densities at −0.3 V(j-0.3 V) were 7.1 and 1.8 mA cm−2, respectively. The results indicated that Au–CeO2/C had great anti-poisoning effect on CO and was a more stable catalyst than E-TEK Pt/C for glycerol oxidation in the presence of CO.

In addition, Siqueira et al. [229] was the first group to report the application of polyvinyl pyrrolidone (PVP) as reducing and capping agents for Au NPs synthesis in electro-oxidation process. They also combined PVP-Au NPs with CNT to create thin films on the indium tin oxide (ITO) using layer-by-layer (LbL) method. The result revealed that PVP-Au NPs/CNTs LbL films covered the entire ITO surface homogenously, and positively enhanced the magnitude of the anodic currents in glycerol electro-oxidation. The prepared sample demonstrated great potential for application in practical fuel cells. Fig. 12 describes the preparation method and LbL structure of the Au NPs/CNTs.

3.1.2. Pt-based catalysts

In one of the early studies in this field, Gomes et al. [230] investigated the effect of single crystals of Pt on the electrochemical oxidation of glycerol in low potentials (0.05 V). Pt (1 0 0) and Pt (1 1 0) surfaces favored the breaking of the C–C–C bond while these surfaces were poisoned at high potentials. However, Pt (1 1 1) surface did not favor the breaking of C–C–C bond and it was more active in oxidation of glycerol due to less poisoning by glycerol dissociation residues. In another study, Zuo et al. [231] constructed a rational design and synthesized a dendritic Pt (1 1 1) facet based on nano-materials with enriched edge and corner atoms as a catalyst for electro-oxidation of glycerol. The Pt (1 1 1) facets are considered as the most active catalysts for glycerol oxidation. Thus, the final catalyst was a highly crystallized Pt nano-flowers on the Tellurium (Te) nano-wires as a template.

The procedure for the galvanic replacement reaction with H2PtCl6 is described in Fig. 13. In detail, 1 mM H2PtCl6 (pH = 7) was added into the mixture solution of as-prepared Te nano-materials and CTAB [232] (Fig. 13a (step 1)). Consequently, PtCl62− was reduced to Pt atoms, forming an uneven discrete distribution of Pt@Te nano-shell on the surface of the Te nano-materials [233]. Then, Te atoms in the Te@Pt hetero-structure was dissolved and the Pt source around Te nano-materials could quickly capture the electrons from the oxidation process of Te → TeO2 [232,234]. The newly formed Pt atoms were deposited in a special manner in the presence of CTAB, resulting in a hollow hetero-structure (Fig. 13b) [235,236]. As the reaction continued, the driving force for the reaction dropped and un-reacted Te atoms would be dissociated, owing to the Kirkendall effect and generated porous Pt nanotubes (steps 2). However, if another 700 μL of H2PtCl6 was injected into the solution, the aggravation of the galvanic replacement reaction would stimulate the decomposition of the hollow hetero-structure, and the newly formed Pt atoms would adhere to the previous ones with Te atoms, which preferred an island growth mode [237,238] (Fig. 13 step...
than the commercial Pt/C catalyst (0.07 A mg⁻¹) than the commercial Pt/C catalyst (0.07 A mg⁻¹).

After a few initial studies on application of supported monometallic Pt/C sample in electro-catalytic oxidation of glycerol, researchers came out with a novel idea related to the application of bimetallic samples to enhance catalytic activity and stability. Consequently, Siomes et al. [212] synthesized various supported Pd/C, Pt/C, Au/C and bimetallic Pd-Au/C, Pd-Ni/C nano-catalysts. The activities of bimetallic samples were as follows: Pd₀.₃-Au₀.₇/C > Pd₀.₃-Pt₀.₇/C > Pd₀.₅Ni₀.₅/C. Even the activities of non-Pt based catalysts (Pd₁-Cu/C and Pd₀.₅-Ni₀.₅/C) for glycerol electro-oxidation were observed to be similar to the Pt/C catalyst. The substituent of 50% of Pd with Ni atoms could enhance the catalytic activity and decrease the catalyst preparation cost significantly. Siomes et al. [210] extended their study by utilizing bismuth (Bi) instead of Au and Ni for modification of Pd and Pt bimetallic catalysts. They synthesized five different catalysts (Pd/C, Pd₀.₉Bi₀.₁/C, Pt/C, Pd₀.₉Bi₀.₁/C, and Pd₀.₉Pt₀.₅Bi₀.₁/C) by a colloidal route. The characterization results revealed that Bi did not alloy with Pt and Pd. Instead, Bi interacted with the Pd and Pt surfaces. However, the catalyst activity of Bi modified samples was enhanced considerably. Samples activity were in the order of Pd/C < Pt/C = Pd₀.₉Bi₀.₁/C < Pd₀.₉Bi₀.₁/C = Pd₀.₅Pt₀.₅Bi₀.₁/C. The main products were GLY, DHA, and TARA with low potentials but surging the electrode potential led to formation of Mesoxalate (MOX).

In a study by Garcia et al. [239], two electrodes Pt (1 1 1) and Pt (1 0 0) used for electro-oxidation of glycerol in an acidic media. The results revealed that three products were produced (GLYLD, GLYCA, and DHA) on the Pt (1 1 1) electrode, while only GLYLD was detected through the application of Pt (1 0 0) electrode. The reason for the different electro-oxidation of glycerol was due to the different binding modes of dehydrogenated glycerol to the two surfaces. Dehydrogenated glycerol binded to the surface through two single Pt-C and one double Pt=C bonds by application of Pt (1 1 1) and Pt (1 0 0), respectively. Proposed reaction mechanism (Fig. 14) suggests two different active intermediates of initial glycerol dehydrogenation on the Pt surface: an enediol-type intermediate binding with two adjacent C atoms to the Pt(1 1 1) surface, and an intermediate binding through a single primary C to the Pt(1 0 0) surface. Different bonding modes to the Pt(1 1 1) and Pt(1 0 0) surface have been attributed to the different coordination numbers of their Pt surface atoms, allowing only single Pt–C bonds on Pt(1 1 1) but favoring a double Pt–C bond on Pt(1 0 0). The enediol-type intermediate is similar to the intermediate of the GLYLD-DHA isomerization reaction and serves as a precursor to the formation of both GLYLD and DHA on Pt(1 1 1). However, the intermediate favored on Pt(1 0 0) yields only GLYLD as soluble product. In addition to these two active intermediates, stripping experiments was suggested the existence of a third “inactive” intermediate, which was formed from glycerol, GLYLD as well as DHA. The only oxidation product observed from the stripping of this adsorbate is CO₂. DFT calculations suggest that this species is the most stable adsorbate on Pt (1 1 1), but it does not have a soluble counterpart, in contrast to the two “active” intermediates. GLYCA is oxidized by cleavage of C–C bond to FA and GLA. The production of FA is considered on the basis of the online electrochemical mass spectroscopy (OLEMS) results, which showed that CO₂ is a product of the glycerol electro-oxidation, and on the basis of the HPLC results, in which FA was identified as a product of GLYLD oxidation on both electrodes. In the pathway of the secondary alcohol oxidation, DHA is further oxidized to HPFA via a four-electron transfer reaction. DHA is very difficult to oxidize to CO₂, explaining the very small amount of CO₂ observed in the OLEMS experiments of DHA oxidation.

One of the initial successful studies in this field has been carried out by Dector et al. [240]. They prepared Pd/C and Pd/MWCNT based electro-catalysts by impregnation for glycerol electro-oxidation in a micro-fluidic fuel cell. The average particle size and lattice parameters of the catalysts were 7.5 and 3.5 nm for Pd/C and Pd/MWCNT, respectively. The electro-catalytic activity of Pd/C and Pd/MWCNT, investigated in 0.1 M glycerol showed that the onset potential for glycerol oxidation on Pd/MWCNT had a negative shift ca. 40 mV compared to Pd/C. The maximum power density obtained was 0.51 and 0.7 mW cm⁻² for Pd/C and Pd/MWCNT, respectively. The results of this work did not only infer that glycerol could be used as fuel in a micro-fluidic fuel cell but also proved its performance was similar to that obtained with other fuels (glucose).

The impact of different catalyst synthesis strategies (e.g. ethylene glycol (EG) reduction, sodium borohydride reduction and impregnation-H₂-reduction) on the metal-support-interaction of Pt/NCNTs in the electro-oxidation reactions of glycerol, formic acid and CO, and the hydrolysis of ammonia borane (AB) was systematically evaluated by Ning et al. [241]. The different characterization results revealed that the synthesis methods drastically affected the electronic property of Pt NPs. Indeed, Pt NPs preferentially interacted with graphitic nitrogen in EG reduction method due to the electron donating property of graphitic nitrogen, while preferentially interacted with pyridinic nitrogen and defects in the impregnation-H₂-reduction method due to the vacancies containing NPs favoring the charged metal ion adsorption. The catalytic activity strongly depended on the electronic property of Pt NPs, which can be ascribed by the binding energy of Pt₄7/2(0) from XPS. The pivotal influence of synthesis method on the Pt NPs electronic property was because of the different formation mechanisms of Pt NPs during the synthesis as well as the metal support interaction (MSI) between Pt and nitrogen groups finely tuned the electronic property through the different electron donation-acceptance between Pt and graphitic/pyridinic nitrogen. In an earlier study, the same group reported the MSI between

Fig. 13. (a) Schematic synthesizes procedure of galvanic replacement from Te NWs to Pt nano-flowers with the equivalent charge reaction process, (b) Pt and Te nano-shell on the surface of the Te nano-wires, and (c) Pt nano-flowers [234].
Pt NPs and NCNTs is higher than between Pt NPs and pristine CNTs. In fact, by changing the nitrogen amount of NCNTs and introducing oxygen groups, the electron enrichment of Pt NPs can be tuned. As a result, superior catalytic activity was achieved over Pt/NCNTs in the oxidation of glycerol and electro-oxidation of CO, compared with conventional CNTs as support [242].

Xie et al. [243] also fabricated different Pt supported catalyst namely Pt/porous poly-aniline (PANI), Pt/PANI and Pt/C. The Pt/porous PANI hybrid nano-structure, fabricated by attapulgite (ATP) as the sacrificial template, registered the best activity. When the ratio of \( \frac{m_{\text{Au}}}{m_{\text{ATP}}} \) was 1:3 and reaction time of removing template was 11 h, the Pt/porous PANI catalyst exhibited excellent electro-catalytic activity (4.6-fold of Pt/PANI) toward glycerol oxidation.

3.1.3. Pd-based catalysts

Previously, Pd is mentioned as the second noble metal widely used in electro-catalytic oxidation of glycerol. The study by Wang et al. [238] reported application of carbon nitride and graphen (CNx/G) hybrid support instead of the conventional bulk carbon for Pd NPs in electro-oxidation of glycerol in 0.5 M NaOH aqueous solution. Fig. 15 clearly exhibits the GLYCA selectivity significantly surged by 10–15% while decreasing the FA selectivity by 15% over the Pd-CNx/G compared to the Pd-CB catalyst. The enhancement in the C3 products toward the Pd-CNx/G catalyst was attributed to the smaller Pd NPs compared to the conventional Pd-CB sample. The interaction between Pd NPs and nitrogen atoms played an important role in the enhancement of selectivity of C3 products. Furthermore, in the study conducted by Kang et al. [244], co-existence of phosphorous and nickel oxide improved the Pd performance in a composite catalyst (Pd-NiOx-P/C).
High electro-catalytic activity of the prepared catalyst was dependent on the high electrochemically active surface area (EASA) value (576.3 cm$^2$/mgPd), fast charge transfer kinetic (Tafel slope value = 68.0 mV/dec) and relatively low activation energy value (EA = 21 kJ/mol).

Next, a Pd core-shell nano catalyst (FeCO@Fe@Pd/C) was tested for electro-catalytic oxidation of ethanol, EG, and glycerol [245]. The best results were reported for oxidation of EG due to its faster electro-catalytic rate constant ($k_{cat}$) when compared to the glycerol (2 times) and ethanol (4 times). The onset potential for ethanol was 110 mV and 230 mV higher than EG and glycerol, respectively. The ratios of forward to reverse peak current densities ($j_f/j_b$) values were 1.28, 2.81 and 2.33 for ethanol, EG, and glycerol, respectively. This suggests that ethanol oxidation had poisoned the catalyst. The peak current density ($i_p$) of the core-shell was between 3.9 and 4.7 higher than the Pd/C monometallic catalyst. Finally, the Pd core-shell nano-catalyst was very stable against catalyst poisons even after 200 cycles. In order to determine the performance of Pd catalysts with different supports, impedance spectroscopy (EIS) and CA techniques. The obtained results and economical impacts significantly.

High electro-catalytic activity of the prepared catalyst was dependent on the high electrochemically active surface area (EASA) value (576.3 cm$^2$/mgPd), fast charge transfer kinetic (Tafel slope value = 68.0 mV/dec) and relatively low activation energy value (EA = 21 kJ/mol).

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The objectives of these studies were to synthesize and prepare a catalyst without application of noble metals for reducing environmental and economical impacts significantly. For example, Oliveira et al. [247] used free-noble metal Ni/C and NiCO/C nano-catalysts as electrodes in glycerol electro-oxidation study. The reaction over both catalysts was carried out at potential higher than 1.2 V before the Ni and Co oxo-hydroxides (NiOOH and CoOOH) formed, which have significant effect on product distribution because of the C–C bond cleavage of the original molecule. GLY, glycolate, and formate were the main products and a little amount of TAR and oxalates were detected. The in-situ FTIR measurement also revealed the presence of hydroxyypyruvate ion and CO$_2$ as the reaction products. Large amount of CO$_2$ was formed with NiCO/C nano-catalyst as the electrode material since the cobalt in the nickel based catalyst enhanced the C–C bond cleavage of the glycerol molecules.

Oliveira et al. [248] extended their study in the synthesis of a carbon-supported nickel NPs by impregnation method for serving as the anode catalysts. Parameters such as scan rate, temperature, and concentration of supporting electrolyte and electro-reactive molecule were varied to investigate the electrochemical effect on the glycerol conversion at the surface of the electrode covered by catalytic oxyhydroxide species ($\beta$-NiOOH). In general, the oxidative transformation of glycerol was a limited mass-transport reaction process. Thus, the peak potential and the peak current of glycerol oxidation on Ni/C electrodes shifted with the scan rate and temperature variation, which are the characteristic of an irreversible diffusion-controlled phenomenon. This reaction start in the beginning of the transformation of $\beta$-Ni(OH)$_2$ species to $\beta$-NiOOH. The glycerol oxidation on $\beta$-NiOOH layer is strongly dependent on the OH– concentration. Formate was the main product at higher glycerol concentrations, while at lower glycerol concentrations, carbonate and oxalate prevailed.

Another novel concept recently reported in electro-oxidation of glycerol is the simultaneous in-situ formation of a homogenous precursor solution Ni-based catalysts using sodium tartrate and PVP as dispersant or protector at the anode and cathode for glycerol oxidation and hydrogen evolution, respectively [249]. The formation of electro-catalysts and their immobilization on the electrode surface occurred simultaneously, avoiding the tedious and laborious procedures. Ni salt in the homogeneous solution was deposited to repair the Ni-based electro-catalysts on the electrode surface, accompanied by the electro-oxidation of glycerol at the anode and the hydrogen evolution reaction at the cathode, exhibiting good working stability. This technique may find potential applications in the conversion of solar energy into storable fuels via the electrolysis of H$_2$O or small molecules to produce hydrogen.

3.2. Bi-metallic based catalysts

Recently, various research groups reported synthesizing some state of the art and novel bimetallic samples for electro-oxidation of glycerol. Dash and Munichandraiah, [250] prepared a series of poly (3,4-ethylenedioxythiophene) (PEDOT) supported Pd-Ru nano-flower samples. The Pd$_2$-Ru-PEDOT/C electrode was highly sensitive toward glycerol detection with sensitivity of 99.8 MA/Cm$^2$µM$^{-1}$ and LOD of 0.1 µM. Zalineera et al. [251,252] synthesized two series of catalysts including a self-supported Pd$_4$Bi and Pd$_4$Sn$_x$ samples with porous nano-structure of $S_{BET} = 75–100$ m$^2$/g and $S_{SUR} = 25–80$ m$^2$/g, respectively. Results revealed that aldehyde, ketone, and carbohydrate species were produced at low potentials, while hydroxyypyruvate at moderate and CO$_2$ and CO$_2$ at high potentials. Also, the catalyst experimental runs inferred Sn could significantly reduce the required potential from 0.6 V to 0.45 V in electro-oxidation of glycerol.

Wang et al. [224] and Gomes et al. [253] tested the Au-Ag/C bimetallic catalyst in their study and reported that Ag addition has led to the performance of glycerol oxidation reaction at lower potentials. Ag could also change the reaction pathway of glycerol electro-oxidation by breaking the C–C–C bands and formation of FA. The main reasons for significant impact of Ag on the bimetallic catalyst (Au-Ag/C) activity are electronic modification and Ag segregation on the catalyst surface.
Jin et al. [255] further investigated the surface modification of Ag NPs supported on reduced graphene oxide (RGO) with a small amount of Au and the activity of Au-modified Ag/RGO (AuₓAgₓ/RGO) catalysts. CV measurements indicated that the AuₓAgₓ/RGO catalyst registered almost the same activity as Au/RGO in terms of the geometric surface area of glassy carbon substrates for glycerol oxidation in alkaline solution, while Ag/RGO exhibited no catalytic activity. The AuₓAgₓ/RGO catalysts have great advantages over Au/RGO in terms of the Au mass specific activity.

In a different study by Holade et al. [255], various experimental parameters influencing the straight forward NPs synthesis by Bromide Anion Exchange (BAE) method was investigated. They synthesized two bimetallic Au-Pt/C and Au-Pd/C samples as advanced surfactant-free NPs for anode electrodes design in abiotic or hybrid glucose biofuel cell. Most importantly, this method drastically changed the structure of Au-Pd nanostructures to alloyed system when Au atomic content was higher than 50%. The activity test results revealed that GLY and glycolate ions were the main products of glycerol conversion in alkaline medium on Pt NPs when bromide ion to metal (s) molar ratio was 1.5, with a cumulative selectivity higher than 80%. The BAE constitutes a promising and suitable chemical route for fuel cells electrode materials preparation with the combination of high chemical synthesis yield (minimizing metal loss), good active surface areas and unexpected catalytic electro-activities.

A series of bimetallic Pd-Au/C electro-catalysts were synthesized in different ratios (100:0, 75:25, 50:50, 25:75, and 0:100), using the borohydride reduction method [256]. CV which was assisted by ATR-FTIR in-situ and chronoamperometry (CA) experiments revealed that the addition of Au remarkably enhanced the electro-catalytic activity. The highest current density (≈ 4 mA mg⁻¹metal) was achieved for the Pd₅₀Au₅₀/C and Pd₇₅Au₂₅/C catalysts, twice more than that achieved by Pd/C (2 mA mg⁻¹metal) demonstrating the beneficial effect of Pd-Au alloy. In addition, Mougenot et al. [257] used plasma supporting method for the first time in preparation of different Pt free bimetallic catalysts (PdₓAuₓ/C, PdₓAgₓ/C and Auₓ/C) and reported that plasma supporting method improved the bimetallic samples activity compared to the conventional wet chemistry method because of electrode structure and surface composition.

Unfortunately, there are limited numbers of studies on electro-oxidation of glycerol in the base-free or acidic environments with the studies performed using carbon supported catalysts only. One of the initial attempts in base-free environment was carried out by Kwon et al. [258] who for the first time reported almost 100% selectivity to DHA using Pt/C electrode in a Bi saturated solution. The main purpose of this study was to evaluating Bi presence in the solution and compared the performance with Pt-Bi/C electrode, previously conducted by Simoes et al. [210]. The results confirmed the researcher’s hypothesis that the highest activity could be achieved by constant and full coverage of Bi on Pt/C surface. Bi in acidic medium has led to glycerol oxidation to DHA on a Pt/C electrode. In fact, Bismuth blocks the active sites for primary glycerol oxidation, reduce the onset potential, and increase the activity by forming a Bi-related active site on the surface ready for secondary oxidation. The obtained result (100% DHA selectivity) surpasses the 25–30% selectivity of DHA in alkaline environment [238].

As Fig. 16 illustrates, primary alcohol oxidation leads to the formation of GLYLĐ and GLYCA, the latter species being subsequently oxidized to GLA and FA. FA has been shown to be the species leading to the formation of CO₂. However, FA may also easily dehydrate on Pt to give rise to adsorbed CO, and this is the most plausible pathway for the formation of CO during glycerol oxidation. In the presence of Bi on the surface, GLYLD and GLYCA formation is much reduced, and adsorbed CO is not observed, which indicates that the pathway for primary alcohol oxidation is blocked at several stages. However, there is a clearly enhanced formation of DHA, not only relatively, but also in an absolute sense. It is well-known that Bi blocks the formation of poisonous CO from small organic molecules, such as FA, through a third-body effect.

Pupo et al. [259] synthesized SnₐPtₐ and RhₐPtₐ core-shell electro-catalysts by chemical reduction method. They studied the catalytic activity toward glycerol oxidation in acidic medium. CV analyses suggested the successful synthesis of core–shell structures for Rh@Pt₃ and Sn@Pt₃ catalysts, observed from their similar profiles to polycrystalline Pt. Higher electro-oxidation currents, as well as lowest onset potential for glycerol oxidation were seen for the catalysts with greater amounts of Pt. Characterization results confirmed that core-shell NPs were homogeneously distributed on the carbon black surface. The Sn@Pt₃ and Rh@Pt₃ catalysts presented better features when taking into account the CV, polarization curves, CA, XRD, and TEM data for fuel cells applications. In fact, with high Pt content, the lower onset potential was achieved (130 mV for Sn@Pt₃ and 120 mV for Rh@Pt₃). Thus, the proportion of Pt in the precursor metals presented a positive influence on the catalytic activity. The enhanced catalytic activity could be attributed to the interactions of Pt electronic structure with the core metal.

Hong et al. [260] demonstrated a facile method to synthesize a series of bimetallic Pd-Pt nano-wire networks (NWN) with tuneable compositions. The modified electronic states of Pd and Pt, improved electro-oxidation kinetics of the Pd-Pt nano-crystals, and the synergistic effects between Pd and Pt account for the enhanced electro-catalytic activity of the prepared Pd-Pt nano-crystals. All the prepared Pd-Pt NWNs obviously possessed higher current density than the commercial Pt/C, revealing their superior catalytic activity. The PdₓPt₁₋ₓNWNs sample displayed the highest activity with the peak current value of 0.046 A cm⁻², which was higher than commercial Pt/C (0.023 A cm⁻²). The catalytic activity follows the order:
The synthesized sample was the practical fuel cell operation. The researchers claimed that their synthesized PC-MWNT also registered a current density 1.6 times the Pt/C in a 404.6 mWmgPd.perMEA used as support for Au NPs. The Au/CeO2/PC-MWNT hybrid electro-catalyst was prepared by two approaches of sequential (1.5 nm) supported on 1-Pyrenecarboxylic acid functionalized MWNTs and alcohol oxidation reaction (ADR) network, (2) Ag-Pd alloy led to accelerate the reaction rate of aldehyde oxidation reaction (ADOR) alcohols namely methanol, ethanol, EG, and glycerol using Pd-Ag/CNT bimetallic catalyst in electro-oxidation of alcohols could be attributed to the following reasons: (1) Ag helped Pd to accelerate the reaction rate of aldehyde oxidation reaction (ADOR) and alcohol oxidation reaction (ADR) network, (2) Ag-Pd alloy led to significant reduction of Ag particle size from 17.7 nm to 2.7 nm without covering the sample surface by surfactant which led to the high electrochemically active surface area (ECSA) of Pd-Ag alloy, (3) Pd-Ag/CNT could cleave the C–C band of long chain polyols which provides high fuel efficiency, and finally (4) CNT with high electrical conductivity, high mechanical and thermal stability formed 3D electrode structure on membrane electrode assembly (MEA) and improve the mass transfer of alcohol and OH−.

Another successful recent study on application of CNTs was reported by Yuan et al. [262]. Their group synthesized a non-Pt based electro-catalyst for glycerol electro-oxidation. The CeO2 nano-clusters (1.5 nm) supported on 1-Pyrenecarboxylic acid functionalized MWNTs (PC-MWNTs) which were prepared by two approaches of sequential polyelectrolyte functionalization and microwave-assisted self-assembly used as support for Au NPs. The Au/CoOx/PC-MWNT hybrid electro-catalyst could achieve tremendous activity and stability with a peak current density 28 times the commercial Pt/C sample. The Au/CoOx/PC-MWNT also registered a current density 1.6 times the Pt/C in a practical fuel cell operation. The researchers claimed that their synthesized sample was the first to report a higher catalytic performance of Au-based catalyst compared to the commercial Pt/C catalyst for fuel cell.

In a study done by Li et al. [263], the application of two non-metallic (Pt/C and Pd/C) and bimetallic (Pt-Au/C and Pd-Au/C) samples for glycerol electro-oxidation was investigated. When Au was added to Pt/C and Pd/C, the values of onset potential (Eonset) were 133 and 139 mV more negative on Pt-Au(wt 4:1)/C and Pd-Au(wt 4:1)/C electrodes than that on the Pt/C and Pd/C electrodes. Also, the value of Eonset for glycerol electro-oxidation on Pt-Au(wt 4:1)/C electrode was 160 mV more negative than that on Pd-Au(wt 4:1)/C electrode. The values of current densities (j=0.3V) on Pt-Au(wt 4:1)/C and Pd-Au(wt 4:1)/C electrodes were 4.6 and 6.2 times larger than Pt/C and Pd/C electrodes.

Prasanna and Selvaraj [264] synthesized a novel ternary polymer-CNT composite by application of three monomers (amine terminated cyclophosphazane (ATCP), hexachlorocyclo-tri-phosphazene (CP), and 2,2’-benzidinedisulfonic acid (BZD)) as support for Pt and Pt-Sn NPs for electro-oxidation of glycerol. The results revealed that Pt/ATCP-CP-BZD-CNT and Pt-Sn/ATCP-CP-BZD-CNT samples deposited considerably higher oxidation current (26.59 mA/mg and 38.89 mA/mg) at lower onset potential (−0.64 V and −0.74 V) than the commercial Pt/C. The prepared novel samples also were stable even for more than 100 cycles. Fig. 17 describes the schematic representations for the preparation of ATCP-CP-BZD-CNT composite and Pt and Pt-Sn NPs deposited ATCP-CP-BZD-CNT composites.

Rezaei et al. [265] decorated the Cu filled nano-porous stainless steel (NPSS) electrode with Pt and Pd (Pt-Pd/Cu/NPSS). The prepared sample gave 4.2 times higher current density (J) at a lower onset potential (Eonset = −0.54) compared to Pd/Cu/NPSS and Pt/Cu/NPSS samples. Pt-Pd/Cu/NPSS also showed 1.3 times more EASA and more poisoning tolerance than the other two single decorated samples. This group expanded their investigations and synthesized another bimetallic (Pt-Au/NPSS) catalyst [266]. The results over this sample also were similar to the previous bi-metallic sample. In fact, the bimetallic Pt-Au nanostructure exhibited higher current density and mass activity (more than 2 times) than monometallic Pd/NPSS and Au/NPSS. The onset potential for Pt-Au/NPSS was lower than that for Au/NPSS and Pd/NPSS.

3.3. Multi-metallic based catalysts

Recently Martines and his coworkers, [237] tested fast polyls method assisted with microwave to synthesize a tri-metallic sample of rhodium (Rh)-decorated Pt NPs with iridium oxides (IrOx) (Rh/Pt/IrOx/C) for electro-catalytic oxidation of glycerol. The results confirmed that Rh could improve the electro-chemical stability of catalyst by preventing agglomeration effects. These NPs were possible to decorate a posterior in a controllable way by a simple electro-chemical protocol. This method provides great opportunities in synthesizing a multi-metallic catalyst in a controlled manner.

The application of tri-metallic or multi component catalyst is rarely reported in this field. However, Do Valle et al. [267] prepared a trimetallic Pt–Ru–Sn, Ru–Sn–O/Ti catalyst for electro-oxidation of glycerol by thermal decomposition of polymeric precursors. The oxidation of glycerol enhanced significantly in the presence of RuO2 and SnO2 due to the larger surface area and ability to donate large amount of OH species. The Pt0.8Ru0.2Sn0.5O/Ti sample depicted approximately 170 mV less positive than PtO2/Ti samples. Rostami et al. [268] also synthesized the electro deposited Pd-Co layers on Au electrode. The maximum current density of Pd-Co(3)/Au sample was approximately twice larger than the Pt/Au. The difference confirmed the positive role of Co in improving the catalytic activity of Pd on Au surface. Pd-Co(3)/Au also informed 8 mV lower onset potential compared to Pd/Au and Co could enhance the poisoning tolerance of Pd during the electro-oxidation reaction. Pd-Co(3)/Au exhibited high activity even after 200 cycles.

3.4. Non-metallic based catalysts

Hickey et al. [269] used a combination of an enzymatic oxalate oxidase and an organic oxidation catalyst (4-amino-TEMPO) for complete oxidation of glycerol to CO2. Initially, various commercially available derivatives of TEMPO were evaluated using CV at pH 7. TEMPO-NH2 indicated the highest catalytic rate of 1453 μA cm−2 8 times more than catalyst rate over unmodified TEMPO (282 μA cm−2). The complete electro-chemical oxidation of glycerol by TEMPO-NH2/oxalate oxidase (OxO) was out performed in bulk electrolysis of a solution coating both enzymatic and organic catalyst at pH 5.2. Consequently, the current density was as high as 1.2 mA cm−2 and the reaction products in 22 h reaction time were GLYCA, TARA, Mesoxalic acid, and glyoxylic acid. C NMR analysis also confirmed the presence of a peak corresponding to C-enriched CO3− at ca. 165 ppm with a peak intensity of 90.6C.

3.5. Summary

Even though there are limited numbers of research studies on electro-chemical oxidation of glycerol reported in literature [26,27], the knowledge related to the electro-catalytic oxidation of glycerol have expanded significantly during the last five years which reflected the
importance of value-added chemicals such as DHA, GLYCA, MA, and TARA from a bio-renewable source such as glycerol. Similar to the catalytic oxidation of glycerol, the electro-chemical reaction could also be performed in both alkaline and base-free environments. The majority of electro-catalytic oxidation of glycerol studies has been performed in the alkaline environment but only few in acidic or neutral (base-free) environments. The electro-chemical approach showed great advantage compared to the conventional catalytic process. With the new approach one has better control of the desired products selectivity when the reaction is performed in aqueous media with low reaction temperature and pressure. The application of polymer supports or the combination of polymers and other supports such as carbon have attracted more attention recently. The main reasons are the utilization of more environmental friendly materials and reduction of catalyst preparation costs by utilizing cheaper materials in synthesizing an active and selective catalyst for electro-chemical oxidation.

4. Concluding remarks and recommendations

One of the ways for achieving low carbon living is to produce value-added chemicals by the catalytic transformation of bio-sustainable resources employed as substitutes for fossil fuels. Value-added chemicals from glycerol have raised great interests due to its huge availability as a waste by-product from the biodiesel industry. Its effective utilization will be one of the key factors in future bio-refineries and could significantly promote biodiesel commercialization and development. Indeed, producing biomass-derived chemicals from glycerol is a global challenge. The high cost of industrial grade glycerol limited the economic viability of its transformations, except for products used in the high value niche markets; i.e. cosmetic additives, tanning agent components, amino acid precursors, or selective metal chelants. Consequently, as the price of glycerol decreases, new products, especially polymers, will be increasingly derived from glycerol.

This review presents various catalytic and electro-chemical processes for oxidation of glycerol into useful chemicals and materials. Special emphasis was given to the effect of different noble-metals, supports and parameters influencing the selectivity and yield for specific glycerol derivatives. Indeed, various factors that have been evaluated as the most influential parameters on the glycerol oxidation reaction conversion, product distribution, product selectivity, and catalyst long-life stability are (1) the presence of NaOH in reaction medium, (2) application of different catalyst preparation methods such as impregnation, sol-immobilization, incipient wetness, and deposition precipitation which could control the particle size of metal NPs, (3) basic or acidic characteristics of support, (4) influence of sample structure on modification of metal NPs, (5) application of various capping agents, and finally (6) application of bi- or multi-metallic NPs instead of mono-metallic samples.

Recent breakthroughs in catalyst synthesis and characterization led to unprecedented achievements in this field. Despite advances in this field, there are still many challenges for increasing selectivity and yield. Thus, a clear direction for utilization of recent novel ideas, methods, and materials could significantly improve knowledge in this field. Consequently, researchers are presented with excellent opportunities in catalysis and nano-materials to design highly active catalysts for glycerol oxidation to specific useful products. The methods of catalyst preparation (e.g. impregnation, sol-immobilization, incipient wetness, and deposition precipitation) greatly influenced the catalyst activity and selectivity. Indeed, all the catalysts that were synthesized by sol immobilization produced fine metal NPs with highly homogeneous distribution on the support and effectively controlled the selectivity of the desired products.

Oxidation-assisted polymerization of glycerol presented a new field of polymerization in aqueous media assisted by oxidation and could be applied to general polyhydroxy compounds. The process is very new and yet it has achieved acceptable results in the recent few years. A new system of chemistry in developing modern oleo-chemistry using glycerol as renewable resources is inevitable. The search for hybrid homogeneous–heterogeneous systems that are stable at both acidic and basic pH is actively investigated. The use of different supports for base and acid catalyst encapsulation could increase diffusion and catalyst activity. Water-resistant homogeneous–heterogeneous catalysts are needed as glycerol normally contains some water. Synthesis of new hybrid materials will improve the distribution of the active sites to enhance catalytic activity. Oxygen species present on the catalyst surface has high value and could lead to higher glycerol conversion rates.
Various products for energy or H₂ production such as TAR, DHA, HPY and MOXAL can be obtained from the glycerol oxidation reaction. For example, TAR involves the oxidation of primary alcohol groups, a relatively straightforward approach to achieve on Pt-based catalysts. The DHA and HPY products involve the oxidation of the secondary alcohol group into a ketonic group. Although all the challenges, it has been successfully reported in alkaline media on Au-based catalysts. Moreover, product separation and purification steps are also important aspects on which studies should be focussed.

The photo-catalytic process is a novel and promising strategy in glycerol oxidation reaction under milder reaction conditions and with altered selectivities, compared with the conventional thermo-catalytic route. As reported in this review limited numbers of research groups are working on the photo-catalytic oxidation of glycerol and definitely it requires more efforts and attention in the future particularly application of novel heterogeneous catalysts not only TiO₂ but also other semiconductor materials with more suitable band edge energies, as well as visible light assistance process of glycerol oxidation using direct plasmonic photo-catalysts (DPS) which showed promising results and should be investigated more intensively in the future. Nevertheless, further research efforts have to be devoted in this field in order to understand the reaction mechanisms and optimize the activity/selectivity parameters. The combination of selective glycerol oxidation with hydrogen generation via photo-catalysis evidence that practical applications can be achieved ensuring a more sustainable future.

Application of different catalysts in electro-chemical oxidation of glycerol in a solid polymer fuel cell or in a solid polymer electrolysis cell was discussed for the cogeneration of energy and value-added chemicals. In-situ infrared spectroscopy measurements and HPLC analyses of oxidation products have shown that the product distribution can be controlled through catalyst composition and structure and through the applied electrode potential. All these insights foresee the possibility to enhance the activity of the catalysts and to control the selectivity of desired products in glycerol electro-oxidation reaction. Studies on synthesizing an electro-catalyst to control glycerol oxidation to desired product, without cleavage of the C=O bond, is new, and therefore should be developed. One of the main goals is then to considerably increase the selectivity towards a given product by both catalyst and potential effects.

Inevitably, cost-efficient production approaches of the glycerol oxidation products would open new markets for the products in the petrochemical industry, which were restricted due to currently high production costs. One of the most important factors in this context is synthesizing non-precious-metal-containing catalysts which exhibited promising results and could be suitable alternatives to noble-metal based catalysts, which are still in the very early stages of investigation. Indeed, some of the reported novel catalysts hold promise to be valuable catalysts if the selectivities toward single products can be further tuned. The economic aspect of glycerol oxidation should in general be kept in mind when exploring new active catalysts. However, fundamental research always allows investigating new reaction pathways to ensure a gain in knowledge and give the chance to discover unprecedented reaction pathways.

Indeed, the ideal goal in future bio-refineries would be transformation of crude-glycerol, which contains impurities like methanol, residual homogeneous or heterogeneous catalysts, and other salts, to valuable products. Finding active and stable catalysts which can catalyze the reaction in crude glycerol will be a huge step forward in applying these catalysts in industry. However, this issue is rarely investigated and only a few reports can be found in the literature. It will significantly reduce the biodiesel production costs as well as different environmental concerns. Hence, researchers should focus more on utilization of crude-glycerol to determine how to control the effect of various impurities in crude glycerol on the desired products selectivity and catalytic activity in oxidation process. Besides the fundamental aspects, where great progress has been achieved over the last years, this last challenge should not be neglected by the researchers in this field.

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