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Hydrogenolysis and carbonylation of glycerol to value-added chemicals: A review article

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Abstract
Glycerol is a potential starting material for the synthesis of value-added chemicals due to the presence of the three hydroxyl groups. The catalytic transformation of glycerol *via* hydrogenolysis and carbonylation has attracted attention due to the production of chemicals such as 1, 2-propanediol, 1, 3-propanediol and glycerol carbonate. The products and reaction mechanisms associated with hydrogenolysis and carbonylation of glycerol in the presence of catalysts will be presented in this review. This review will also highlight the challenges associated with glycerol valorization.

Keywords: glycerol, hydrogenolysis, carbonylation, reaction mechanism, catalysts

Introduction

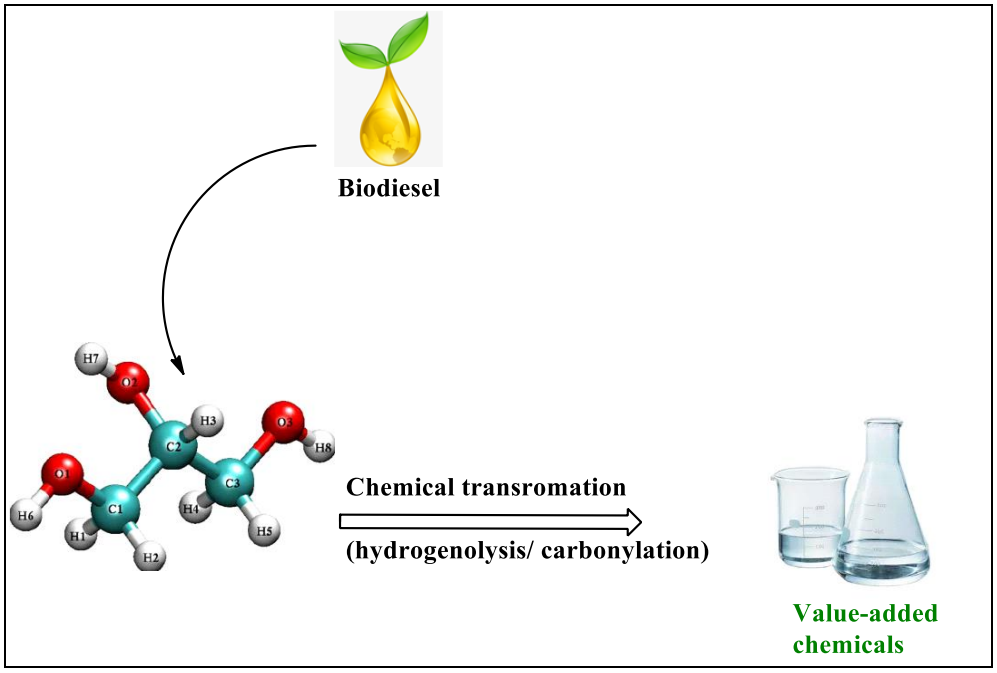
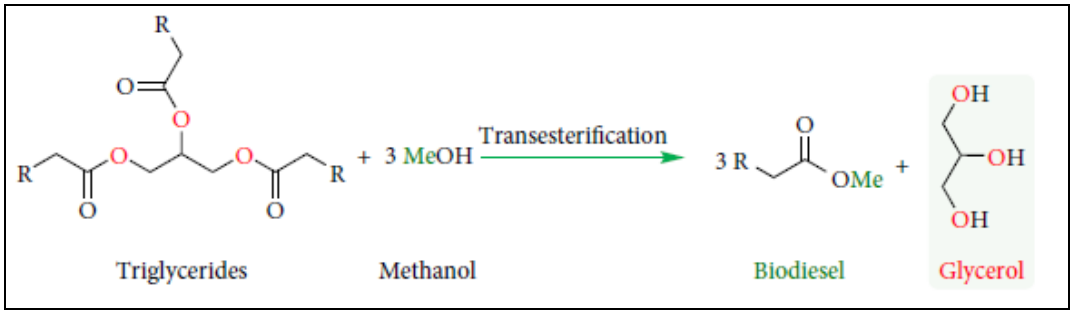


Fig 1

The increase in energy demand has also increased the production of biodiesel as an energy source [1-3]. During the production of biodiesel, glycerol is a co-product due to the transesterification of vegetable oil with methanol (Scheme 1) [4, 5]. As the production of biodiesel increases so does the production of glycerol which requires chemical transformation to value-added products and chemicals. Hydrogenolysis of glycerol involves the breaking of the C-OH chemical bond in glycerol and simultaneous addition of hydrogen to form 1, 2-propanediol and 1, 3-propanediol which have been used as preservatives, antifreeze agents and cleaning agents [6]. The formation of 1, 3-propanediol is less thermodynamically stable than 1, 2-propanediol due to the steric hindrance effect hence the selective production of 1, 3-propanediol is a great challenge [7]. Transition metal catalysts (Cu, Ni and Co) and noble metal catalysts of Ag, Pt and Ru have been used for the hydrogenolysis reaction of glycerol [8-10]. A bimetallic catalyst of Cu-Mg supported on silica was used for the hydrogenolysis of glycerol to 1, 2-propanediol and had a glycerol conversion of 89.5 % and selectivity of 92.1 % for 1, 2-propanediol selectivity [11]. Another study by Pudi, showed a glycerol conversion of 71.6 % and 92.8 % selectivity towards 1, 2-propanediol over a Cu-Ni bimetallic catalyst at 210 ºC and a hydrogen pressure of 4.5 MPa [12].



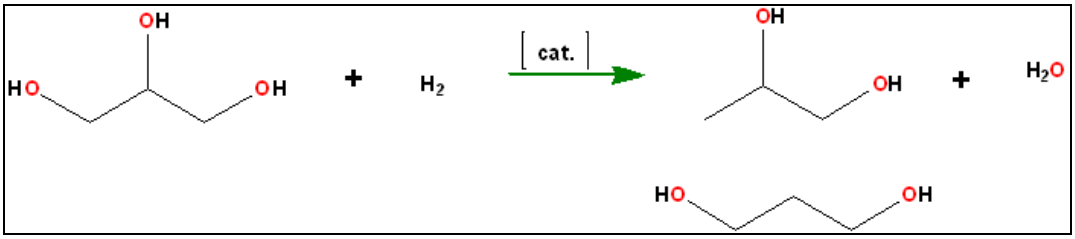
Scheme 1: Catalytic transesterification of triglycerides to biodiesel and glycerol [4].

Glycerol valorization through glycerol carbonylation process is another approach to produce value-added chemicals. Glycerol carbonylation produces glycerol carbonate which has a variety of applications including production of glycidol. Glycerol carbonate is a very useful chemical in the cosmetic and chemical industry due to its properties such as low flammability, low odour, low toxicity and versatile reactivity [13, 15]. According to Magniont and co-workers, in-cooperation of glycerol carbonate in a pazzolanic matrix as an alternative binder improves strength, hardening and reduces shrinkage [16]. There are many ways to produce glycerol carbonate which are dependent on the carbonyl source including urea [17, 18], carbon dioxide (CO_2) and any other organic carbonyl source [19, 21]. The carbonyl source influences the synthesis route of glycerol carbonate [22] and the use of CO_2 as a direct synthesis route is more interesting for it being a green chemistry approach.

At present, most reviews describe in detail the urea chemical route of glycerol carbonylation but there are few reviews that focus on the refined classification of catalysts in direct carbonylation of glycerol with CO_2 and glycerol hydrogenolysis including the plausible mechanisms involved in these reactions. This review focuses on direct glycerol carbonylation using CO_2 to glycerol carbonate, hydrogenolysis of glycerol and mechanisms involved in these reactions. Finally, several challenges aimed at valorization of glycerol are discussed.

Hydrogenolysis of Glycerol

The conversion of glycerol to propanediols through hydrogenolysis assumes selective dehydroxylation of the triol followed by the cleavage of C-O bond followed by hydrogen addition (Scheme 2). The design of the catalyst is a key factor in the transformation process as it requires a catalysts which are selective between C-O and C-C bond breaking.

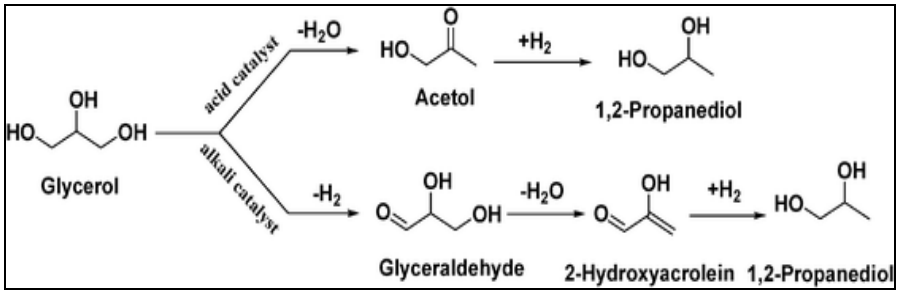


Scheme 2: Hydrogenolysis of glycerol to 1, 2-propanediol and 1, 3-propanediol

A study by with different acidic (V_2O_5, ZrO_2, and TiO_2) and basic (CaO and MgO) oxide-supported copper–zinc bimetallic catalysts by Pandey showed 98. 5% glycerol conversion and 89 % selectivity towards 1, 2-Propanediol Production [23]. Another study by Lee showed 65 % conversion and 98 % selectivity over Cu-supported catalyst [24]. Cu–Cr catalyst was evaluated for the hydrogenolysis of glycerol in both isopropanol and water as solvents at a H_2 pressure of 7 MPa and showed 91 % selectivity to 1, 2-propanediol [25].

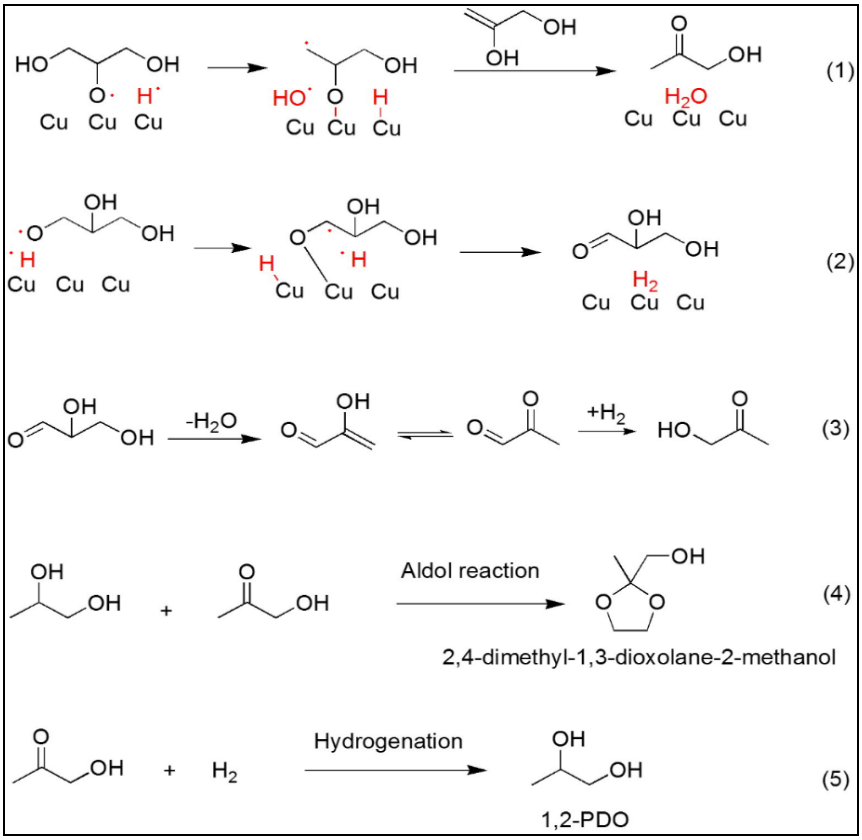
Zhang and co-workers revealed that steric hindrance and electronic configuration in Pt and Ir based nanostructured catalysts are critically important for tunable selectivity towards 1, 3-propanediol during glycerol conversion [26]. This was also confirmed by Wang who synthesized a pseudo-single atom Pt catalyst on mesoporous WO_x for hydrogenolysis of glycerol to 1, 3-propanediol. The results showed high selectivity towards 1,3-propanediol which was attributed to the heterolytic dissociation of H_2 at the interface of Pt and WO_x and the bond formation between glycerol and WO_x which stabilizes the formation of a secondary carbocation intermediate [27]. Liu and co-workers also revealed that Ir-ReO_x catalysts also have a high selectivity for glycerol hydrogenolysis to 1, 3-propanediol [28]. Luo and co-workers carried out glycerol hydrogenolysis to 1, 3-propanediol over Ir-ReO_x and achieved 60.9 % glycerol conversion [29].

Glycerol hydrogenolysis can occur in the presence of basic and acid reaction mixtures which are influenced by variation of catalysts support. According to Balaraju and co-workers (Scheme 3) dehydrogenation of glycerol leads to glyceraldehyde, and it subsequently dehydrates to hydroxyacrolein and further hydrogenation forms 1, 2-propanediol on the metallic sites. Catalysts with acidic supports forms acetol intermediate which is further hydrogenated 1, 2-propanediol [32].



Scheme 3: Proposed glycerol hydrogenolysis mechanism over acid or base catalysts [32]

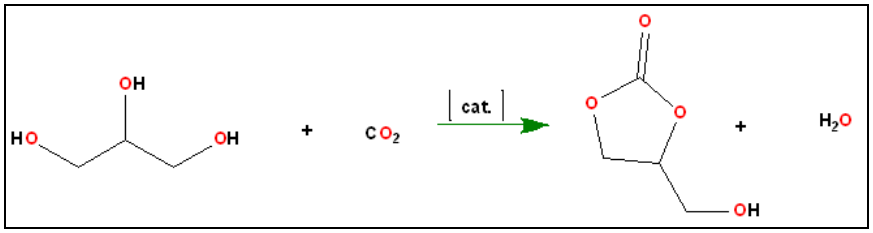
The mechanism to produce 1,2-propanediol from glycerol *via* acetol intermediate (Scheme 4) was proposed by Gao and co-workers who synthesized a Cu-ZnO for the hydrogenolysis of glycerol at a temperature 250 ºC and pressure of 2.0 MPa [30]. According to their GC-MS studies, the reaction happens over the Cu-catalyst surface (Scheme 4; Equations 1 and 2) and some condensation products such as 2, 4-dimethyl-1, 3-dioxolane-2-methanol (Scheme 4; Equation 4) formed through the aldol reaction of acetol. A review by Liu emphasized that to elucidate glycerol conversion mechanisms the role of theoretical density function theory must be emphasized [31].



Scheme 4: Proposed mechanism for the hydrogenolysis of glycerol to 1, 2-propanediol.

Carbonylation of glycerol with CO_2 to glycerol carbonate

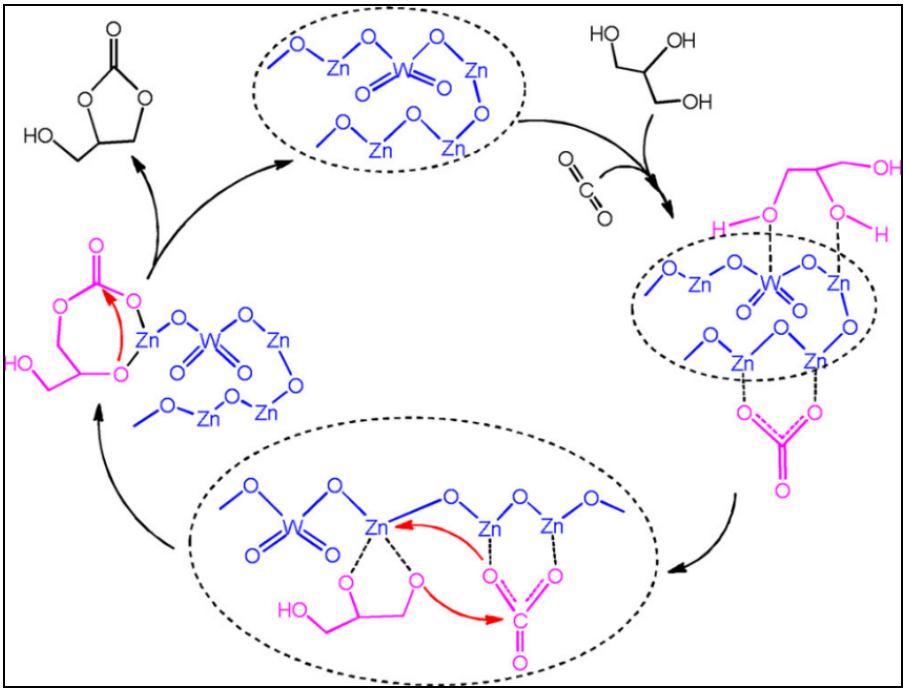
The utilization of CO_2 as a feedstock is an important are in sustainable chemistry and climate change. The rising levels of atmospheric CO_2 have been linked to global warming which has been a great area of concern. The advances in glycerol carbonylation with CO_2 to produce glycerol carbonate is an attractive process because it converts two waste products into value added chemicals (Scheme 5) [33].



Scheme 5: Direct glycerol carbonylation with CO_2 to glycerol carbonate in the presence of a catalyst.

A study carried by Zhang and co-workers on synthesis of glycerol carbonate and monoacetin from the reaction of glycerol and CO_2 in the presence of CH_3CN using Cu supported catalysts (Cu/CaO, Cu/MgO, Cu/La_2O_3, Cu/Al_2O_3, Cu/ZrO_2 and Cu/Mg-Al-Zr) revealed that the particle size and the acid-base properties of catalysts affect the yield of glycerol carbonate [34]. Another study by Li also revealed that the production of glycerol carbonate is also affected by the presence of halogen anions such that the introduction of a halogen anion increases catalytic activity towards formation of glycerol carbonate [35]. The chemical industry is still struggling to design heterogeneous catalysts which can valorize glycerol and CO_2 effectively and efficiently. Kulal and co-workers were successful in designing Zn-doped CeO_2 nanorods for direct glycerol carbonylation with CO_2 and under optimized conditions they achieved 90.4 % glycerol conversion and 89.5 % yield towards glycerol carbonate [36]. Keogh and co-workers synthesized 20 wt% $NaAlO_2/Al_2O_3$ catalysts for the synthesis of glycerol carbonate from glycerol and achieved 96 % yield after 60 min [37].

Li synthesized a novel $ZnWO_4$-ZnO catalyst for the direct carbonylation of glycerol with CO_2 in the presence of DMF at 150 °C and proposed the reaction mechanism shown by Scheme 6 [38]. According to Scheme 6, insertion of glycerol and CO_2 into $ZnWO_4$-ZnO produces zinc glycerolate and a bridged bidentate carbonate species respectively. The insertion of bridged bidentate carbonate into a zinc glycerolate results in the formation of a Zn-seven-member cyclic metal carbonate followed by formation of glycerol carbonate through intramolecular nucleophilic attack of the alkoxy oxygen atom to carbonyl carbon atom.



Scheme 6: The possible mechanism for the synthesis of glycerol carbonate from glycerol and CO_2 in DMF solvent over $ZnWO_4$-ZnO [38].

The valorization of glycerol to value-added chemicals depends on numerous factors such as selectivity of the catalyst, pH of the reaction medium, particle size and pore size of the support for the heterogeneous catalyst [39]. Homogeneous catalyst which have been utilized for the carbonylation of glycerol to glycerol carbonate have been reported to have separation challenges between the reactants and the desired products [40]. Though the direct carbonylation of glycerol to glycerol carbonate is an attractive reaction, it has thermodynamics limitations which cannot be solved by designing an efficient catalyst but by modifying the method including adding dehydrating agents [41].

In general catalytic performance is still a major challenge in the catalytic conversion of glycerol to its derivatives [42, 43].

Conclusion and Future Perspective

Glycerol is a by-product in the production of biodiesel and the production depends on global demand, environmental impact and economy at large. The utilization of the by-products, glycerol and atmospheric CO_2 is a great strategy and process affects global change and environmental effects. Catalysts applied in the valorization of glycerol depend on their design, efficiency, selectivity and separation with the products. On an industrial scale, the process of glycerol valorization must be cost effective. The hydrogenolysis of glycerol to 1, 2-propanediol is a viable process depending on the market due to high selectivity and glycerol conversion. On the other hand, the production of 1, 3-propanediol still has challenges due to poor selectivity and lack of insight in the mechanisms involved. In the future, novel catalyst and reaction conditions still needs to be developed to achieve high yields and selectivity of the desired products of glycerol valorization.

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Authors Contribution
The author wrote, read and approved the final version of the mini-review article.

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