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Review

Sustainable value-added C_3 chemicals from glycerol transformations: A mini review for heterogeneous catalytic processes

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ABSTRACT

It is of importance to convert glycerol, the primary by-product from biodiesel manufacturing, to various valuable C_3 chemicals, such as acrolein *via* dehydration, lactic acid, 1,3-dihydroxyacetone *via* oxidation, and 1,3-propanediol, allyl alcohol *via* hydrogenolysis. As compared to petroleum-based resources, C_3 chemicals from glycerol provide a benign, sustainable and atomically economic feature. Extensive heterogeneous catalysts have been designed, prepared and tested for these transformations. In recent five years, great progress, including high yields to target products over appropriate catalysts, insight into reaction mechanism and network, has been achieved. The present review systematically covers recent research progress on sustainable C_3 chemical production from catalytic glycerol transformations. We hope that it will benefit future research on transformations of glycerol as well as other polyols.
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1. Introduction

Glycerol, also known as 1,2,3-propanetriol or glycerin, is the simplest triol. It is a colorless, odorless, viscous, sweet-tasting and non-toxic liquid. Glycerol is primarily obtained (about 90%) as the main by-product from biodiesel manufacture, while other synthetic routines are followed as well, although typically leading to cost-ineffective processes [1,2]. As biodiesel annual production increases in the past two decades, a large amount of surplus crude glycerol has been generated, which usually needs purification for utilization [3,4]. The current leading applications of glycerol include drugs and pharmaceutical manufacturing, personal care products, polyols and polyether, food, *etc.* Remarkably, catalytic transformations of glycerol produce extensive valuable C_3 chemicals, *e.g.* acrolein, 1,3-dihydroxyacetone and 1,3-propanediol [2,5,6]. With the carbon-atom economy advantage, these C_3 chemicals provide a promising approach to valorize biodiesel manufacture. Catalyst design for these processes are challenging since efficient catalysts should break or form desired O—H, C—H and C—O bonds while keeping C—C bonds intact.

Prior publications reviewed strategies for general glycerol conversion [5] or a particular target product (*e.g.* lactic acid [7], acrolein [8], propanediols [9]), while in the present work, we focus on reviews of catalyst design, reaction mechanism and pathways for various value-added C_3 chemical production from glycerol transformations over heterogeneous catalysts.

2. Classification of Glycerol Conversion to C_3 Chemicals

Since the present review only focuses on C_3 chemicals from glycerol conversion, any transformation containing C—C bond formation or cleavage, *e.g.* glycerol transesterification (monoglyceride) [10], carbonxylation (glyceride carbonate) [11], aromatization (C_6 —C_8 hydrocarbons) [12], oligomerization (C_6 —C_9 di- and tri-glycerol) [13] and reforming (H_2, CO and C_1—C_2 hydrocarbons such as methane and ethylene, short-chain oxygenates such as acetaldehyde and acetic acid) [14], are not covered here.

Before more details are discussed, glycerol conversions to C_3 chemicals are classified into three categories on the basis of C, H and O atom numbers of each component. The formula of glycerol, as a fully saturated oxygenated hydrocarbon, is $C_3H_8O_3$. Glycerol dehydration products have formula $C_3H_{8-2n}O_{3-n}$, where n = 1 or 2, *i.e.* $C_3H_6O_2$, C_3H_4O). Using H and O atom numbers as x and y axes respectively, these two formulas are plotted in Fig. 1, leading to a *dehydration line* (in blue). For comparison, note that two additional formulas, including $C_3H_8O_3$ (glycerol) and C_3H_2 as glycerol dehydration product by removing three H_2O molecules, are plotted along the line, although C_3H_2 is not experimentally reported. The area above the dehydration line is defined as oxidative area, referring to more

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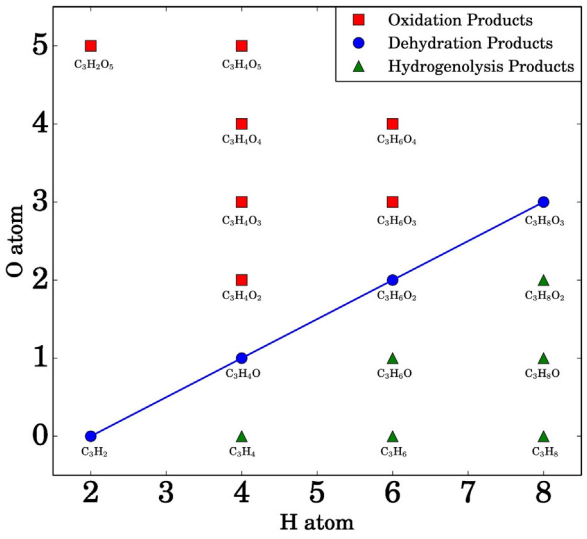


Fig. 1. Classification of glycerol transformations into C_3 chemicals: oxidation, dehydration and hydrogenolysis products.

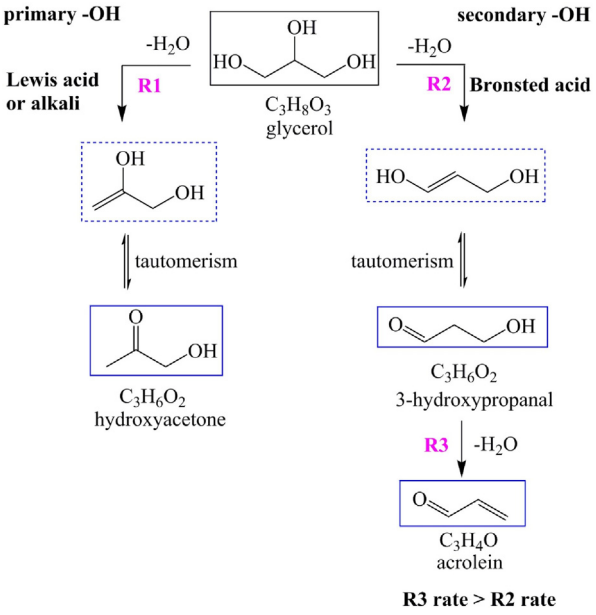


Fig. 2. Glycerol dehydration network, blue: dehydration products; solid frame: experimentally found products; dash frame: proposed intermediates.

O atoms for a given H atom number, or less H atoms for a given O atom number, as compared to formulas on the line. Similarly, the area below the dehydration line is defined as hydrogenolysis area. In the following sections, glycerol transformations are discussed in terms of dehydration, oxidation and hydrogenolysis, respectively.

3. Glycerol Dehydration

As shown in Table 1, three (3) C_3 compounds, including hydroxyacetone, 3-hydroxypropanal and acrolein, have been reported as glycerol dehydration products [20,28,29]. At *ca.* 300–400 °C, gas-phase glycerol dehydration has been performed over alkaline (La_2CuO_4 [15], La_2O_3 [30]) or acidic catalysts (microporous or mesoporous zeolite/molecular sieves such as ZSM-5 [16], MCM-41 [24], SBA-15 [31] and metal oxides such as WO_3 [25]). As shown in Fig. 2, when dehydration of glycerol occurs at the primary or secondary hydroxyl (—OH) groups, two enols (alkenols) are directly generated (steps R1 and R2), followed by formation of two ketos *via* the well-known keto-enol tautomerism, leading to hydroxyacetone and 3-hydroxypropanal, respectively. Hydroxyacetone has been reported as a final product with 78% maximum yield [17] from glycerol dehydration, while 3-hydroxypropanal is typically converted to acrolein *via* further dehydration (step R3), hence usually not reported as a final product (maximum yield < 1% [32]). As compared to step R2, the reaction rate of step R3 is likely faster, indicating that any product *via* intermediate 3-hydroxypropanal is challenging, as discussed for 1,3-propanediol production in later sections. The pathways of glycerol dehydration to hydroxyacetone and 3-hydroxypropanal/acrolein are competitive, where the former one is promoted by Lewis acid or alkali, while the latter is favored over Brønsted acid. Remarkably, for acid-promoted glycerol dehydration, dehydration activity does not only depend on the strength of acidity, yet is also influenced by types of acid, *i.e.* Brønsted and Lewis. By both experimental and theoretical investigations, Foo and co-workers [28] demonstrated that the selectivity of hydroxyacetone is linearly correlated well with Lewis acidic sites, while acrolein is correlated with Brønsted acidic sites. Similar reports were previously published elsewhere [20,21,29].

4. Glycerol Oxidation

As shown in Table 2, ten (10) C_3 compounds, including glyceraldehyde, 1,3-dihydroxyacetone, glyceric acid, pyruvic aldehyde, acrylic acid, hydroxypyruvic acid, pyruvic acid, lactic acid, tartronic acid and mesoxalic acid, are reported as glycerol oxidation products [33,44,65,69]. General oxidation of glycerol includes special oxidation (*i.e.* addition of O atoms) and dehydrogenation (*i.e.* removal of H atoms). As shown in Fig. 3, general glycerol oxidation typically starts with two types of reactions: dehydrogenation (cleavages of C—H and O—H bonds) and dehydration (cleavages of C—H and C—O bonds) followed by additional dehydrogenation and special oxidation (formation of C—O and O—H bonds). The main difference between initial dehydration and dehydrogenation is cleavage of C—O bond, which typically requires different reaction temperatures (300–400 °C for dehydration [29,70], <100 °C for dehydrogenation [34,45]). Since these two subcategories, oxidation *via* dehydrogenation or dehydration as initial steps, exhibit different mechanisms, they are discussed separately in the present section.

4.1. Glycerol oxidation via dehydrogenation

Under oxidative conditions, noble metals (*e.g.* Pt [45,71], Pd [33,35] and Au [38,46,48], *etc.*) are commonly used for glycerol dehydrogenation, owing to their supreme performance for cleavages of C—H and O—H bonds [69], although certain non-noble metal or even non-metal catalysts were also reported in the literature [72]. These transformations are performed at low temperature (<100 °C) in liquid acidic [39] or alkaline solutions [36], although recent work focused on neutral solutions [73] as well.

Table 1
C_3 chemicals from glycerol dehydration

Chemical formula	Name	CAS number	Max. yield	Additional references
$C_3H_6O_2$	Hydroxyacetone	116-09-6	78%	[15-19]
$C_3H_6O_2$	3-Hydroxypropanal	2134-29-4	<1%	[20-23]
C_3H_4O	Acrolein	107-02-8	96%	[8,21-27]

Table 2
C_3 chemicals from glycerol oxidation

Chemical formula	Name	CAS number	Max. yield	Additional references
$C_3H_6O_3$	Glyceraldehyde	56-82-6	23%	[33-37]
$C_3H_6O_3$	Dihydroxyacetone	96-26-4	80%	[38-43]
$C_3H_6O_4$	Glyceric acid	473-81-4	72%	[37,44-47]
$C_3H_4O_2$	Pyruvic aldehyde	78-98-8	25%	[41,48-51]
$C_3H_4O_2$	Acrylic acid	79-10-7	57%	[23,29,41,52-54]
$C_3H_4O_4$	Hydroxypyruvic acid	1113-60-6	19%	[34,36,45,55,56]
$C_3H_4O_3$	Pyruvic acid	127-17-3	12%	[41,57-59]
$C_3H_6O_3$	Lactic acid	50-21-5	95%	[49,51,60-64]
$C_3H_4O_5$	Tartronic acid	80-69-3	78%	[36,44,46,47,65]
$C_3H_2O_5$	Mesoxalic acid	473-90-5	30%	[36,56,66-68]

By removing one molecule hydrogen from glycerol, glyceraldehyde and 1,3-dihydroxyacetone are obtained from dehydrogenation at primary and secondary hydroxyl groups, respectively (steps R4 and R16 in Fig. 3). If only noble monometallic catalysts (*e.g.* Pt and Pd) are used for glycerol oxidation [37], primary hydroxyl oxidation species, including glyceraldehyde along with its further oxidation product glyceric acid (step R9) are the main products [45], while when promoters (*e.g.* Bi, Sb) are added into these noble metals, dehydrogenation mainly occurs at secondary hydroxyl, leading to high selectivity towards 1,3-dihydroxyacetone [74]. In principle, if further dehydrogenation occurs at the primary hydroxyl of glyceraldehyde, glucic acid could be generated (step R5 in Fig. 3), while no experimental observation has been reported yet. Similarly, tartronaldehydic acid, which can be obtained either from glucic acid oxidation (step R6) or glyceric acid dehydrogenation (step R10), is not experimentally found, although it was proposed as intermediate [36,71] for tartronic acid (*via* step R7). On the other hand, if dehydrogenation occurs at the secondary hydroxyl of glyceraldehyde, hydroxypyruvaldehyde is produced [66] (step R14), while it may be also derived from 1,3-dihydroxyacetone dehydrogenation (step R17) [36,49,72]. Hydroxypyruvaldehyde is likely thermodynamically unstable, thus, only its oxidative product hydroxypyruvic acid is reported (step R15). Note that glyceric acid dehydrogenation may also produce hydroxypyruvic acid (step R11) or tartronaldehydic acid (step R10) [40]. Further dehydrogenation of tartronic acid leads to mesoxalic acid (step R8) [36,72], the fully oxidized C_3 species from glycerol without losing any O atom. In addition to the tartronic acid pathway (step R8), mesoxalic acid can also be produced from

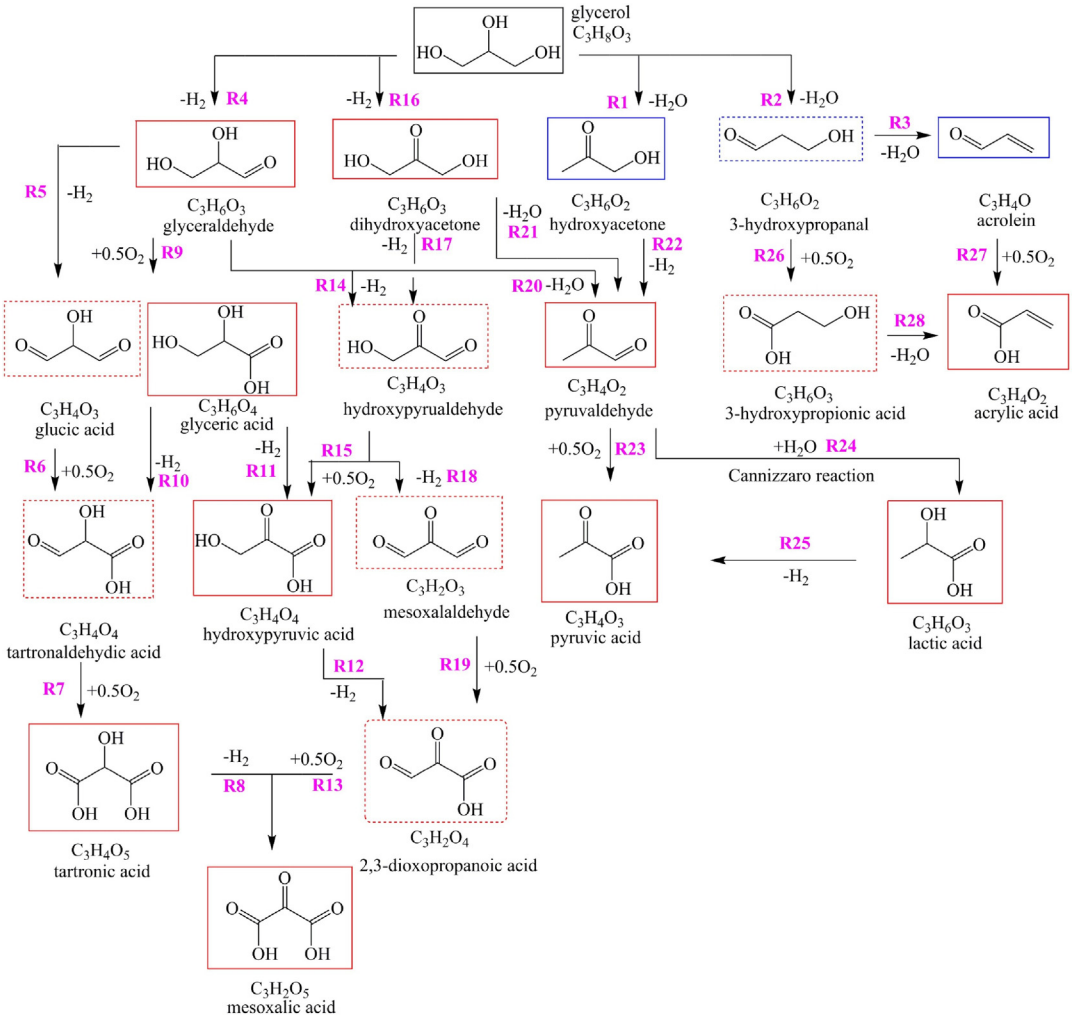


Fig. 3. Glycerol oxidation network, red: oxidation products; blue: dehydration products; solid frame: experimentally found products; dash frame: proposed intermediates.

hydroxypyruvic acid sequential dehydrogenation (step R12) and oxidation (step R13) *via* intermediate 2,3-dioxopropanoic acid [66]. Another possible pathway for mesoxalic acid is *via* hydroxypyruvaldehyde dehydrogenation (step R18) followed by two-step oxidation (R19 and R13).

4.2. Glycerol oxidation via dehydration

Under oxidative operating conditions (*e.g.* molecular O_2 or H_2O_2), dehydration may occur over alkaline or acidic sites, where Lewis acidic [60] or alkaline sites [61,62]) typically lead to hydroxyacetone (step R1 in Fig. 3, the same as in Fig. 2), while Brønsted acidic sites usually generate 3-hydroxypropanal(step R2) [16,24], followed by acrolein *via* further dehydration (step R3). Dehydrogenation of hydroxyacetone produces pyruvaldehyde (step R22) [50], which may be also derived from glyceraldehyde (step R20) or 1,3-dihydroxyacetone (step R21) *via* dehydration over Lewis acids [48-50]. Pyruvaldehyde further converts to an important chemical — lactic acid *via* Cannizzaro hydration reaction (step R24) [49,57,63] over Lewis sites [60]. The highest yield of lactic acid is obtained as 95% over Cu/ZrO_2 [63]. Note that pyruvaldehyde oxidation easily produces pyruvic acid with 12% maximum yield (step R23) [41,57]. Lactic acid dehydrogenation over noble metals (*e.g.* Pd or Pt) may lead to pyruvic acid (step R25) [55], which indicates that dehydrogenation performance should be carefully controlled if lactic acid is the target product. As discussed above, if a catalyst contains Brønsted sites, glycerol typically sequentially dehydrates to 3-hydroxypropanal and acrolein. Note that 3-hydroxypropanal is typically not experimentally observed, owing to the faster reaction rate of glycerol further dehydration to acrolein, its oxidation product 3-hydroxypropionic acid (step R26) is not reported in the literature. Instead, oxidation of acrolein at the carbonyl group leads to acrylic acid [50,75] (step R27), for which moderate oxidative catalysts, such as V [52], Mn [53], Mo [76], W—Mo—V [77], Nb [54] and Fe [58], are employed. Note that dehydration of intermediate 3-hydroxypropionic acid was proposed to produce acrylic acid as well (step R28) [78].

5. Hydrogenolysis of Glycerol

As shown in Table 3, nine (9) C_3 compounds, including 1,2-propanediol, 1,3-propanediol, allyl alcohol, acetone, propanal, 1-propanol, 2-propanol, propylene and propane, were reported as glycerol hydrogenolysis products [9,79,97]. Under hydrogen (*e.g.* H_2) environment, glycerol hydrogenolysis, *i.e.* hydrodeoxygenation, starts with dehydration (cleavages of C—O and C—H bonds) followed by hydrogenation (formation of C—H and O—H bonds) and/or further dehydration to various chemicals. The proposed reaction pathways are shown in Fig. 4. As discussed in the prior section, the initial dehydration step is typically promoted over acidic sites, while Lewis and Brønsted acids lead to dehydration at the primary and secondary hydroxyl groups, respectively.

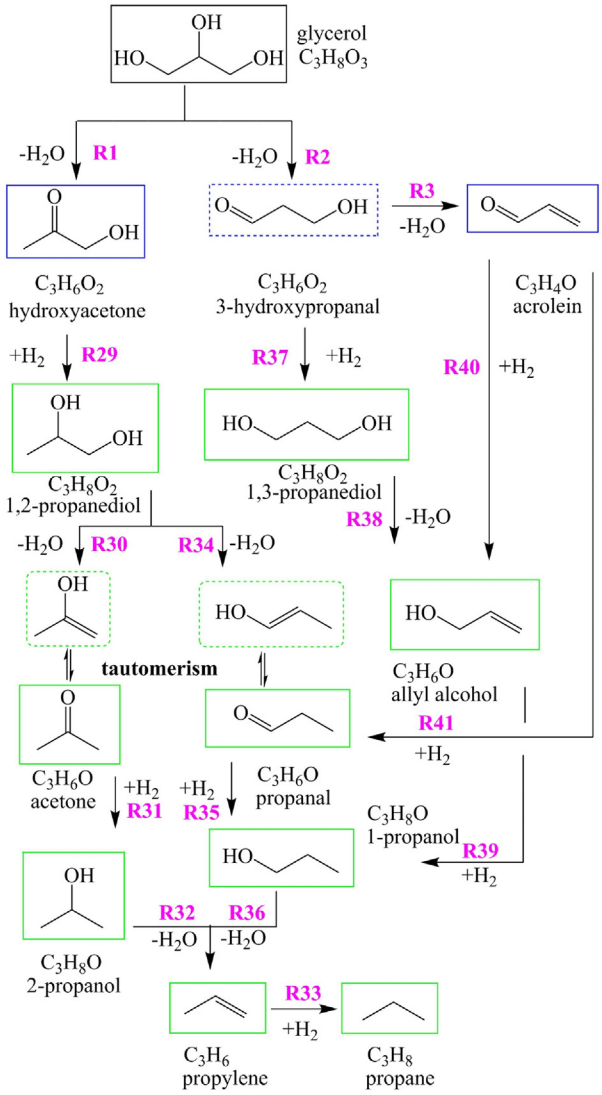


Fig. 4. Glycerol hydrogenolysis network, blue: dehydration products; green: hydrogenolysis products; solid frame: experimentally found products; dash frame: proposed intermediates.

5.1. 1,3-Propanediol, 1,2-propanediol and allyl alcohol

As similar to prior two sections, Brønsted acids promote glycerol dehydration at the secondary hydroxyl, generating 3-hydroxypropanal (step R2 in Fig. 4), which is the intermediate to 1,3-propanediol *via* hydrogenation of the aldehyde group (step R37). Note that 3-hydroxypropanal is mesostable since its further dehydration, also promoted by Brønsted sites, leads to acrolein (step R3). Thus, high selectivity towards 1,3-propanediol is usually limited. Extensive efforts have been focused on efficient catalyst

Table 3
C_3 chemicals from glycerol hydrogenolysis

Chemical formula	Name	CAS number	Max. yield	Reference
$C_3H_8O_2$	1,2-Propanediol	57-55-6	97%	[79-83]
$C_3H_8O_2$	1,3-Propanediol	504-63-2	69%	[67,84-86]
C_3H_6O	Allyl alcohol	107-18-6	91%	[87-91]
C_3H_6O	Acetone	67-64-1	20%	[85,92-94]
C_3H_6O	Propanal	123-38-6	50%	[30,83,95,96]
C_3H_8O	2-Propanol	67-63-0	15%	[93,97-99]
C_3H_8O	1-Propanol	71-23-8	33%	[95,99,102-104]
C_3H_6	Propylene	115-07-1	90%	[103-107]
C_3H_8	Propane	74-98-6	61%	[105,108-110]

designed for improving the selectivity towards 3-hydroxypropanal and 1,3-propanediol [84,85,111]. In general, bifunctional catalysts, including Brønsted sites for the dehydration step and noble metals (*e.g.* Pt [85,86,112], Pd and Ir [100,113]) for the hydrogenation step, are employed for 1,3-propanediol preparation. In fact, once 3-hydroxypropanal is formed under hydrogen environment, two competitive pathways (steps R3 and R37) appear over these bifunctional active sites, *i.e.* 3-hydroxypropanal further dehydration to acrolein over Brønsted sites and 3-hydroxypropanal hydrogenation to 1,3-propanediol over metallic site. To achieve high selectivity to 1,3-propanediol, relatively fast hydrogenation rate and slow dehydration rate, indicating high metal dispersion/high hydrogen pressure and moderate Brønsted acidity, should be followed. The most commonly used and investigated catalyst is Pt/WO_x/Al_2O_3 [85,92,93,98,112], in which Pt serves as hydrogenation site, while WO_x and Al_2O_3 provide Brønsted and Lewis acidic sites, respectively. Interestingly, in principle, Lewis sites are not required to form 1,3-propanediol, while note that they are always unavoidable even over WO_3 that provides extensive Brønsted sites. For example, Au was added into Pt/WO_x to decrease Lewis sites and improve the selectivity to 1,3-propanediol [80]. In addition to types of acidity, the strength of acidity also influences 1,3-propanediol selectivity. Single-atom Pt/WO_x catalysts, which exhibited excellent hydrogenation performance likely owing to atomically dispersed Pt and very low selectivity (about 5%) to 1,2-propanediol owing to relatively low Lewis acid strength, provided 20% selectivity to 1,3-propanediol while 60% selectivity to 1-propanol [114]. As proposed in Fig. 4, this observation implies that too high Brønsted acids may lead to further dehydration of either 1,3-propanediol (step R38) or 3-hydroxypropanal (step R3), both eventually leading to 1-propanol *via* step R39, steps R40 and R39 or steps R41 and R35, respectively. The highest yield of 1,3-propanediol has been improved to 69% over Pt/WO_x catalyst at 180 °C and 5 MPa H_2 for 12 h [84], as most glycerol hydrogenolysis reactions were carried out under elevated H_2 pressure (1–5 MPa) [9,80,85,86,98,112].

In contrast, if a catalyst contains strong Brønsted acids, no noble metal for supreme hydrogenation performance [87], or the reaction was carried without any external H_2 source (hydrogenation may occur *via in situ* H_2 derived from glycerol reforming) [115], allyl alcohol is stably produced from acrolein hydrogenation (step R40). As compared with 1,3-propanediol, 1,2-propanediol is more commonly manufactured as the primary product from glycerol hydrogenolysis (steps R1 and R29). It is obtained from hydrogenation of hydroxyacetone (step R29), the dehydration product at the primary hydroxyl of glycerol as promoted by Lewis acid sites. Typical catalysts include Cu-based materials, while the highest yield of 1,2-propanediol is up to 97% [79,81-83].

5.2. Acetone, propanal, 1-propanol and 2-propanol

The following four C_3 chemicals, including acetone, propanal, 1-propanol and 2-propanol, are usually not target products from glycerol transformations in the literature. They are always co-produced with 1,2-propanediol and/or 1,3-propanediol. As indicated in Fig. 4, further dehydration of 1,2-propanediol at primary and secondary hydroxyl groups, followed by corresponding tautomerism transformations (steps R30 and R34), generates acetone [76] and propanal, respectively. In addition, acrolein was proposed as an intermediate for propanal production in various prior reports (step R41) [22,87,116]. Both 1-propanol and 2-propanol were reported as glycerol hydrogenolysis by-products as well, where selectivity to 1-propanol is (33% maximum yield [100]) typically higher than that for 2-propanol (less than 15% maximum yield) [97,93]. 1-Propanol can be formed from 1,2-propanediol (steps R34 and R35), 1,3-propanediol (steps R38 and R39) or acrolein *via* either propanal (steps R41 and R35) or allyl alcohol (steps R40 and R39) as intermediates [80,85], while 2-propanol is always co-produced with 1,2-propanediol (steps R30 and R31) [117]. These reaction pathways were experimentally confirmed by separately feeding 1,3-propanediol, 1,2-propanediol and acrolein as reactants [93].

5.3. Propene and propane

C_3 hydrocarbons (propylene and propane), as glycerol fully deoxygenated products, were reported over various catalysts, including Ir/ZrO_2/ZSM-5 [103], Pt/ZSM-5 [104], stainless steel [118], Cu/Al_2O_3 [108], Fe-Mo [119] and ZrO_2-FeO_x [115], *etc.* Both 1-propanol and 2-propanol may dehydrate over acidic sites, leading to propylene (steps R32 and R36), while hydrogenation easily occurs under hydrogen environment and certain operating conditions, forming propane (steps R33) [108,109]. The reaction temperature is typically controlled at *ca.* 250 °C in hydrogen environment, which may perform hydrogenolysis (cleavages of C—H and C—O bonds) of glycerol well, while keeping C—C intact. The highest yields for propylene and propane are 90% over Fe/Mo/C and 61% over Ru/C [105], respectively.

6. Conclusions and Prospects for the Future

As may be seen from the present review, glycerol transformation to various valuable C_3 chemicals over heterogeneous catalysts has become a promising approach for glycerol utilization, which valorizes biodiesel manufacture. To reach a high yield of target C_3 products, catalyst design (such as appropriate metal selection, metal dispersion control, type and strength of acids or alkali) and operating conditions should be carefully performed. Looking towards the future, we believe that most current yields of target C_3 chemicals will be further improved. In the near future, we expect that production of various C_3 chemicals from glycerol transformations will be widely commercialized in the chemical industry.

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