

Catalytic Synthesis of Glycerol Carbonate

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Glycerol carbonate (GC) belongs to the family of organic carbonates that are regarded as very typical “green chemistry” products for their unique advantages in many fields, such as high boiling point solvents, pharmaceutical intermediates, and material intermediates.

glycerol

green chemistry

by-product

glycerol carbonate

catalysis

1. Routes for Glycerol Carbonate (GC) Synthesis

There are four main synthetic routes (**Figure 1**) reported at this stage to convert glycerol into racemic glycerol carbonate, namely (1) reaction of glycerol with phosgene, (2) carbonylation of glycerol by urea, (3) transesterification of glycerol with dimethyl carbonate or ethylene carbonate, and (4) reaction of glycerol with carbon dioxide or carbon monoxide ^{[1][2]}.

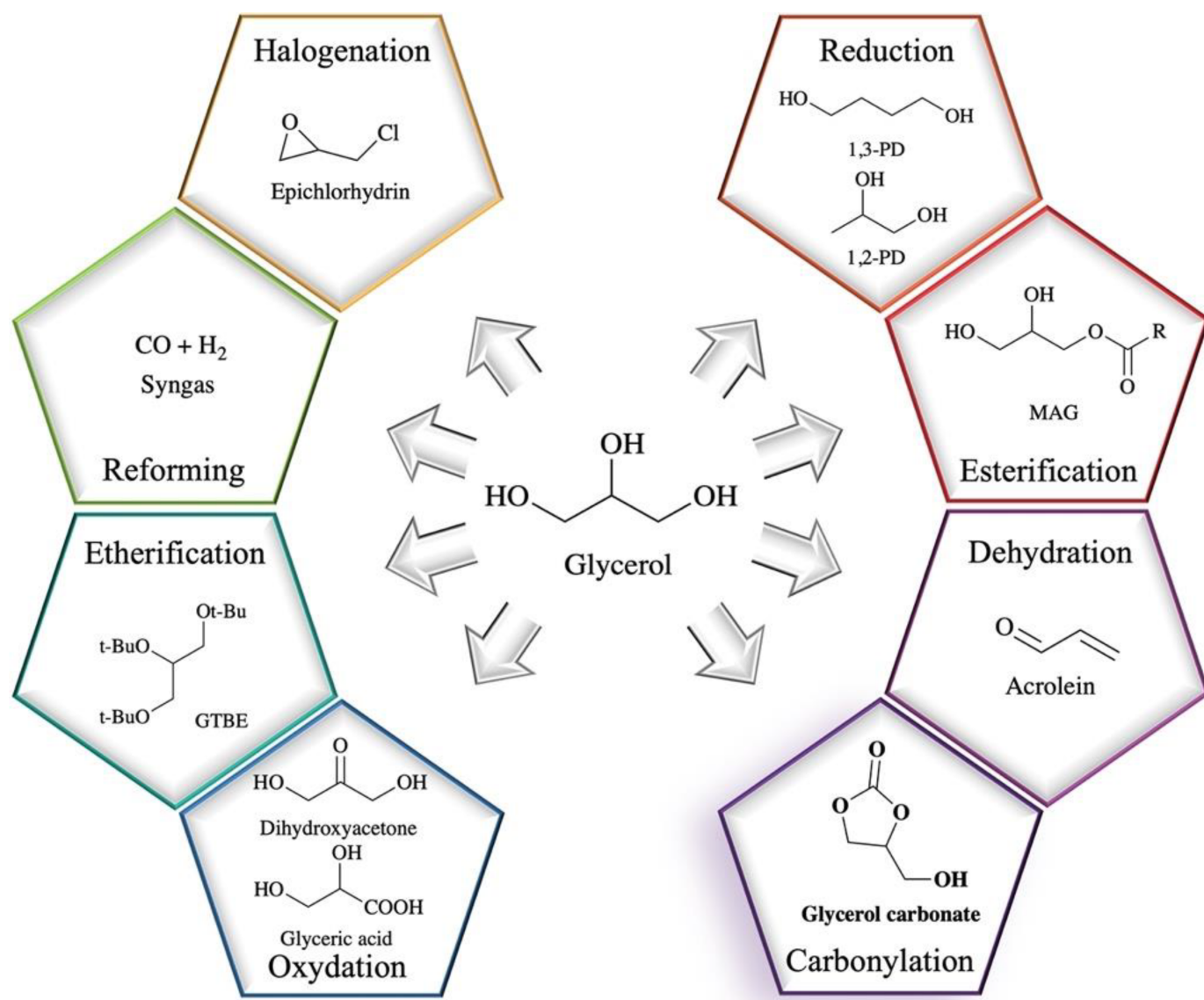


Figure 1. Main synthetic routes to glycerol carbonate.

2. Phosgene Route

As early as 1948, the method to produce glycerol carbonate was developed by Strain [3] by using glycerol and phosgene (Figure 1).

The catalysts used in this route are some common alkali metal salts and alkaline-earth metal salts, such as NaOH, Na_2CO_3 , $\text{Ca}(\text{OH})_2$. Subsequent literature reported that pyridine, which is basic due to the lone electron pair on the nitrogen atom accepting protons, can also catalyze the reaction of glycerol and phosgene to produce GC [2].

Although the phosgene route has good reaction performance, it not only needs to be carried out at a very low temperature ($-70\text{ }^\circ\text{C}$), but also the raw materials are highly toxic chemical products, which are not suitable for transportation and pollute the environment. At the same time, the by-product HCl will corrode equipment, and the

complicated process of preparing glycerol carbonate leads to a long operation cycle, which is contrary to the concept of contemporary green chemical industry and belongs to the elimination process [\[4\]](#)[\[5\]](#)[\[6\]](#).

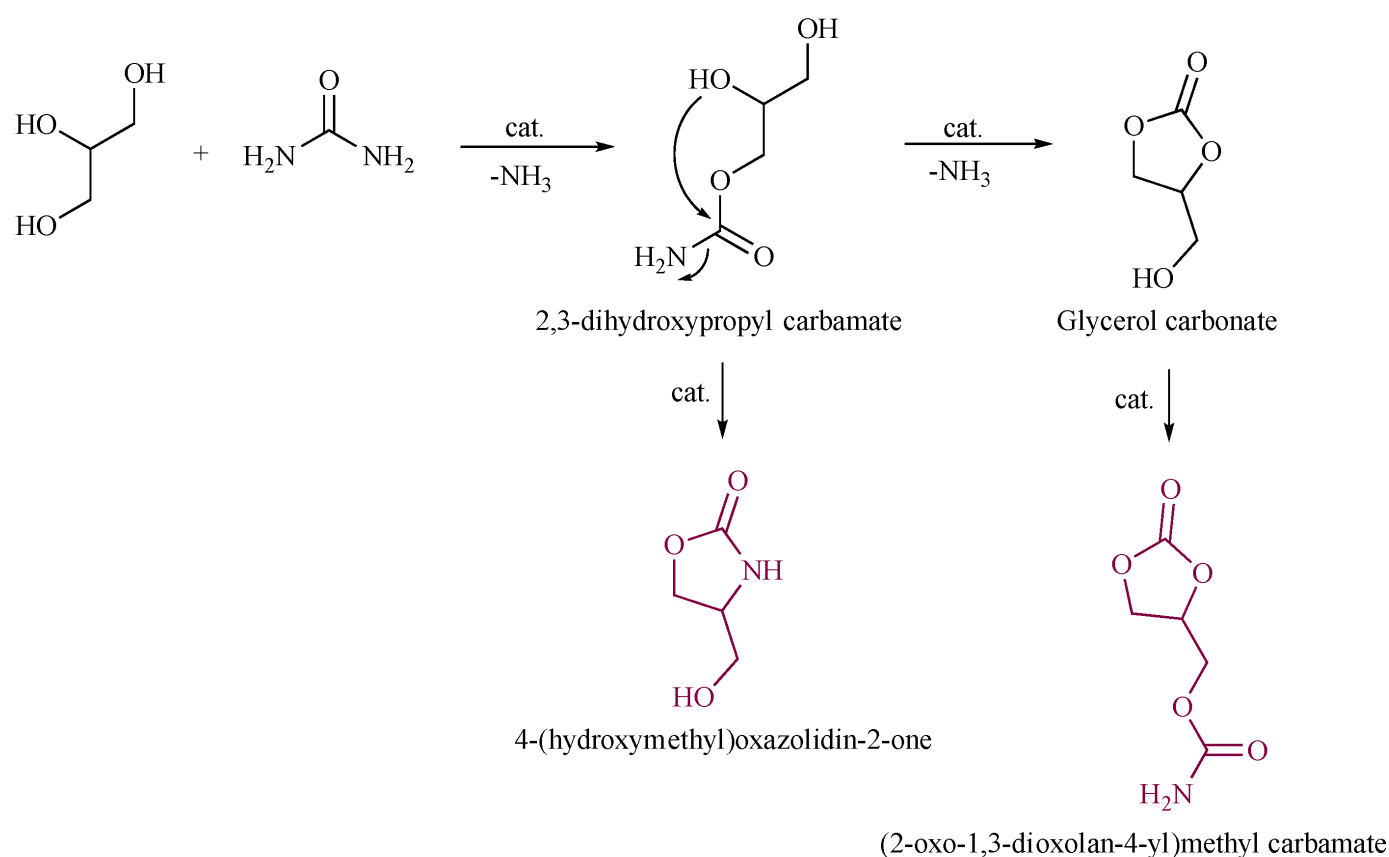
3. Carbonylation by Urea

Synthesis of GC from glycerol and urea in the presence of a suitable catalyst is an attractive method of production, also known as the urea method. The advantages of this reaction system are as follows: the raw materials glycerol and urea are non-toxic, cheap, and easy to obtain, no solvent is added in the reaction, the reaction conditions are mild, and the glycerol conversion rate is high [\[7\]](#).

The by-product of the reaction is only NH_3 , which can be recovered and coupled with CO_2 to generate urea, realizing the indirect synthesis of GC from CO_2 and glycerol. It can be argued that urea represents an activated form of CO_2 . The industrial process utilizes the Bosch–Meiser urea route, developed in 1922 [\[8\]](#). This makes urea a green and good alternative source for carbonylation reactions. [\[9\]](#).

Nevertheless, in order to promote the reaction balance to shift to the right, it is necessary to continuously remove the generated ammonia gas, which will pollute the environment, under reduced pressure (40–50 mbar), thus increasing investment costs.

The reaction mechanism of the urea route has been studied extensively over the past years. Rubio-Marcos et al. [\[10\]](#) proposed that the hydroxyl group of glycerol attacks the carbonyl carbon atom in urea under the action of the catalyst. After the removal of ammonia gas, a ring-closure reaction will occur to produce glycerol carbonate. Nevertheless, the water loss at this stage can result in the formation of 4-(hydroxymethyl)oxazolidin-2-one as side product; furthermore, GC, after its formation, could subsequently react with urea to yield (2-oxo-1,3-dioxolan-4-yl)methyl carbamate, as shown in [Scheme 1](#).



Scheme 1. Rubio-Marcos proposed reaction pathway of urea and glycerol.

Although it is difficult to establish a clear and general reaction mechanism theoretically, some researchers have used infrared spectroscopy and other methods to explore the reaction mechanism in depth. Calvino-Casilda et al. [11] showed through real-time attenuated total reflection infrared spectroscopy that the first step is a fast step, and the second step is a slow step, that is, the step that determines the reaction time. The reaction conditions must be strictly optimized to prevent the GC and urea from continuing to react to form glycerol carbonate carbamate (Scheme 1) [12].

3.1. Catalyst Application of Urea Route

The GC yield of the reaction system with the urea route is low, and a catalyst must be used to obtain a higher glycerol conversion rate [13]. Consequently, the design and selection of catalysts are particularly critical. The following catalysts bearing Lewis acidic sites seem to produce satisfying results with significant yields: manganese sulfate, zinc oxide, zinc sulfate, zinc chloride, metal oxides (CaO , La_2O_3 , MgO , ZrO_2 , Al_2O_3), γ -zirconium phosphate, mixed oxides HTc-Zn derived from hydrotalcite, $\text{Co}_3\text{O}_4/\text{ZnO}$ nanodispersion, gold-supported zeolite ZSM-5 catalyst, lanthanum oxide as a solid base catalyst, polymer-supported ionic liquids, and samarium-exchanged heteropolytungstate [4]. They are mainly divided into the following four categories of catalysts: metal salt, ionic liquid, solid acid or base, and zinc-based solid catalysts (Figure 2).

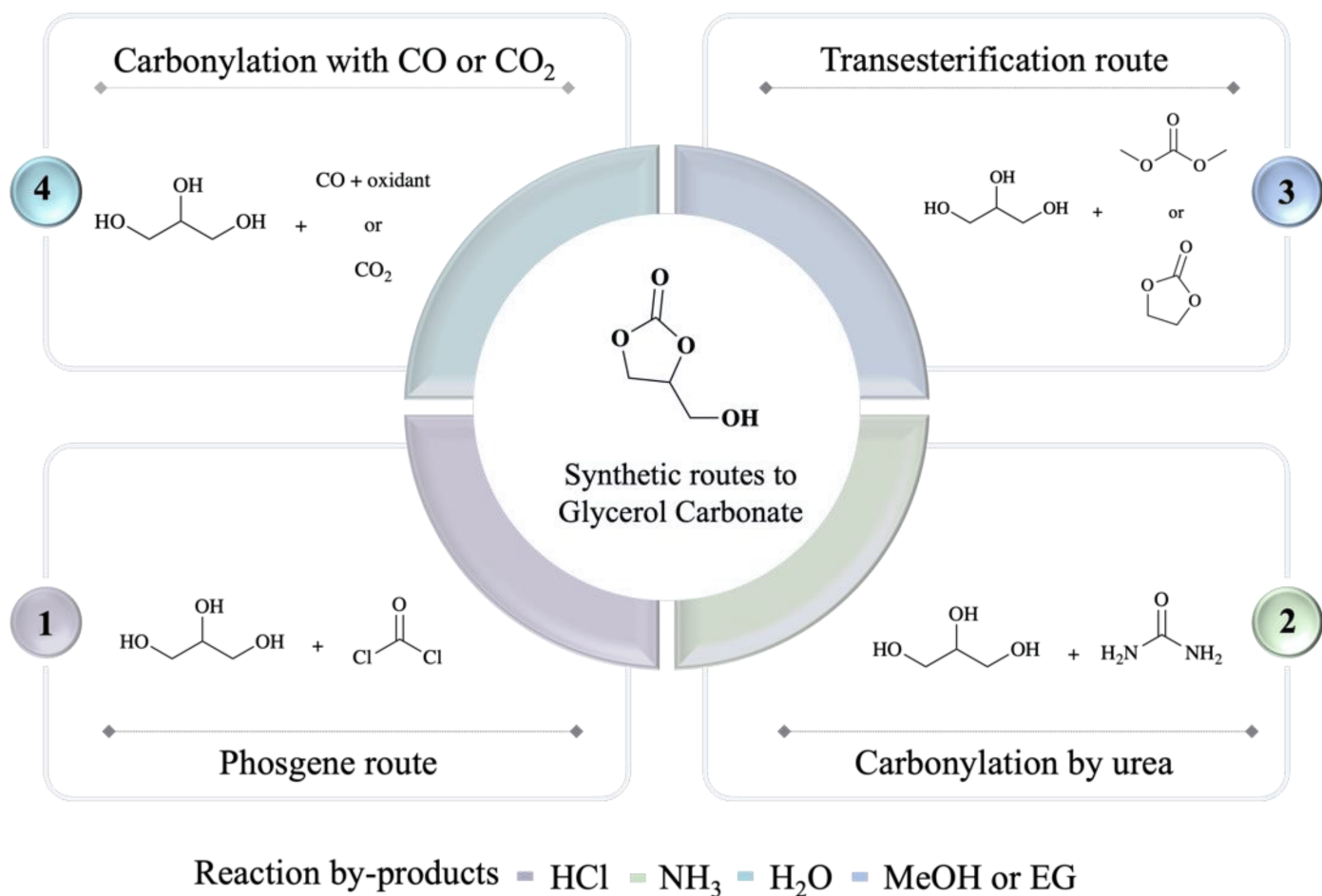


Figure 2. Main categories of catalysts in GC synthesis through urea route.

3.2. The Future of the Urea Route

The glycerolysis of urea represents an interesting synthetic procedure for GC that may have an industrial application. The good conversion of glycerol, the high selectivity, the easy separation of the catalyst and its full recovery, as well as the recovery of NH₃ and the continuous separation of carbonate, make the methodology described very promising.

Among the reported catalysts for this route, the industrial application prospects of zinc-based solid catalysts and solid base catalysts are better [14][15]. At the same time, compared with homogeneous catalysts, heterogeneous catalysts have more research value because they are beneficial to product separation and catalyst recovery.

All in all, in the future development and design of high-efficiency heterogeneous catalysts, the goal should be to achieve the unity of high activity and high stability of the catalyst, and to clarify the role of Lewis acidic-alkaline sites on the catalyst surface in the activation reactants, thereby increasing the conversion rate of glycerol and the selectivity of GC

4. CO Oxidative Carbonylation Route

Carbonylation is a type of reaction in which carbonyl groups are introduced into the framework of organic compounds. This is an important method for preparing carbonyl compounds such as aldehydes and ketones [16]. Carbon monoxide is one of the most important carbonylation reagents. The carbonylation method is used to directly synthesize GC using CO, O₂ and glycerol as raw materials under the action of a catalyst.

The reaction system is generally carried out under the conditions of 0.5–5 MPa and 70–170 °C. The reaction raw materials are cheap and easy to obtain, the reaction by-product is only water, and the atom utilization rate is high. It can also realize the synthesis of the target product in one step without intermediate reaction steps. Under certain reaction conditions, both CO₂ and CO can be used as carbonylation reagents to react with glycerol to generate GC, but compared with CO₂, CO has higher chemical activity. In the reaction of glycerol and CO to produce GC, the most common oxidant is oxygen, which can afford GC in high yield under relatively mild conditions [17].

Therefore, such a route realizes the sustainable conversion of cheap and easily available raw materials into high value-added chemicals.

4.1. The Future of CO Oxidative Carbonylation Route

All things considered, the above-mentioned experimental exploration provide a worthy point of view for future research on the oxidative carbonylation of glycerol to synthesize GC.

In summary, in the reaction process of this route, the most studied catalyst is the metal palladium catalyst, and, among them, the PdCl₂(phen)-KI catalyst system had the best catalytic effect [18][19]. The advantage of this synthetic route is that GC can be generated under relatively mild conditions, the product is easy to separate, the selectivity of the product is high, and the yield is high. However, as CO has certain toxicity and explosiveness, its industrial application is restricted.

4.2. CO₂ Direct Carbonylation Route

Also known as the CO₂ conversion method, it refers to the direct reaction of CO₂ and glycerol under certain conditions to produce GC.

Carbon dioxide is the main greenhouse gas, which is cheap and easy to obtain and non-toxic, while glycerol is a large by-product of the biodiesel industry. If the two are combined to synthesize high value-added chemicals, it will turn double waste into “treasure”, has extremely high environmental value. In addition, the atomic utilization rate of the reaction can reach 87% [20], and the only by-product of the reaction is water, which shows that the reaction system is highly compatible with the concept of atomic economy and green chemistry.

The biggest problem with this route is that it is difficult to break the carbon-oxygen double bond in the CO₂ molecule, which makes the chemical properties of CO₂ highly stable and difficult to activate.

The choice of suitable combinations of catalyst and dehydration agent is crucial to achieving feasible yields in the synthesis of GC from glycerol and carbon dioxide. Usually, quite harsh conditions are necessary with temperatures ranging from 120 °C to 180 °C and pressures varying from 30 bar to 150 bar [21]. Nevertheless, the current research shows that the glycerol conversion rate and GC yield of this route are not high, and the production cost is relatively high.

In order to solve the dehydration problem of the reaction, it was attempted the direct synthesis of GC with glycerol and carbon dioxide under the combined action of 1,8-diazabicycloundec-7-ene/ CH_2Br_2 [22]. This method used mild reaction conditions (70 °C, 1 MPa) and high yield of GC was obtained (86%). However, CH_2Br_2 is toxic and expensive, which hinders the industrial application of this method.

It was reported that the yield of GC could be enhanced when acetonitrile was used as solvent and dehydration reagent in the carbonylation of glycerol and CO_2 . Such as, Podila et al. [23] showed that dibutyltin oxides also catalyze the synthesis of GC, resulting in yields of 7% in presence of acetonitrile. Additionally, in the presence of acetonitrile, La_2O_3 in combination with ZnO or Cu resulted in yields of up to 15% as reported from other research groups [24][25][26].

Although the improved yield was obtained using acetonitrile as the dehydration agent [27], acetonitrile is easily hydrolyzed to acetic acid, which could etherify with glycerol to decrease the yield of GC. The dehydration agent is important for the carbonylation of alcohols with CO_2 . 2-Cyanopyridine was also reported to be an effective dehydration agent [28][29][30]. For example, Liu et al. [31] found it to be effective for the carbonylation of glycerol with CO_2 directly catalyzed by the CeO_2 catalyst. Additionally, as reported by Su et al. [32], it was shown that if 2-cyanopyridine is used as dehydration agent and promoter, a GC yield of 18.7% was obtained without any further additives. Recently, Qiao Zhang et al. [33] described the application of CaC_2 as a dehydrating agent for the direct synthesis of carbamates from amines, CO_2 , and MeOH. Based on the use of CaC_2 , GC was successfully and directly synthesized from glycerol and CO_2 under zinc catalysis and N-donor ligand, in 92% yield. CaC_2 itself is also a sustainable chemical and promotes the transformation of CO_2 into valuable products.

For developing a green methodology, McGregor et al., for the first time, demonstrated the catalytic activities of untreated biochar and biochar ash, catalytic material that can readily be produced from low-value biomass residues, in the synthesis of GC from the reaction of glycerol, acetonitrile, and CO_2 [34].

It was provided novel insights into the behavior of dehydrating agents during the conversion of glycerol in the presence of carbon dioxide and a catalyst [35]. Particularly, they observed that conducting the reaction in the presence of adiponitrile resulted in a five-fold increase in GC yield when compared to acetonitrile, which is currently the most applied dehydrating agent.

In a very recent paper, Hu et al. [36] prepared a cobalt-based zeolitic imidazolate framework-67 (ZIF-67) as a catalyst for the carboxylation of glycerol in the presence of acetonitrile. The conversion, yield, and selectivity achieved with ZIF-67 were 32, 29, and 92%, respectively, conducting the reaction at 210 °C for 12 h. ZIF- 67

exhibited high crystallinity, a high specific surface area, good thermal stability as well as numerous Lewis basic sites, indicating its high catalytic activity.

In recent years, photocatalysis is becoming a hot field as introducing light into the thermally driven reaction system can improve the catalytic performance. He et al. [37] prepared a series of $x\text{La}_2\text{O}_2\text{CO}_3\text{--ZnO}$ catalysts, which were used for the photo-thermal transformation of glycerol and CO_2 into GC. The photo-thermal synergism as well as the cooperation between ZnO and $\text{La}_2\text{O}_2\text{CO}_3$ contributed to its catalytic performance, thus achieving a glycerol conversion of 6.9% under the reaction conditions of 150 °C, 5.5 MPa CO_2 , and 20 mmol g^{-1} with a reaction time of 6 h when 20% $\text{La}_2\text{O}_2\text{CO}_3\text{--ZnO}$ was used as the catalyst.

4.3. The Future of CO_2 Direct Carbonylation Route

Although many researchers have worked on this route, experiments have proved that the direct reaction between glycerol and CO_2 is extremely difficult. This reaction is thermodynamically limited from the production of water during the process; therefore, in order to remove water and to shift the equilibrium towards GC, the use of suitable dehydrating agents has been proposed over the years. Nevertheless, most of the reagents employed to remove water also result in formation of other by-products.

In many experimental examples, the following similar difficulties and problems are encountered: the conversion of glycerol is too low, the carbon dioxide reaction activity is reduced, the reaction needs to be carried out under high pressure conditions, the dehydrating agents are not effective.

Therefore, even if the reaction itself is extremely attractive and important, its application is still very limited. Due to the limitation of thermodynamics, it is impossible to promote the reaction between glycerol and CO_2 simply by developing a new high-efficiency catalyst. Moreover, the method of adding dehydrating agents to move the reaction to the right has very limited effect. In short, for the current research on this reaction system, the development of a more effective reaction system will be the main way to solve the problem.

5. Transesterification Route

In recent years, the transesterification of glycerol and organic carbonates to synthesize GC has attracted attention. The organic carbonates raw materials used are mainly ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC), while the catalysts are mainly inorganic or basic compounds, and lipase catalyst. In the alkaline catalytic environment, during the transesterification reaction, an excess of carbonate is generally added as both a reactant and a solvent, including the most widely used EC and DMC [2]. **Figure 1** above depicts the main process of synthesizing GC through the transesterification reaction of EC or DMC with glycerol.

GC intermediates will be generated during the reaction, and the by-products of the reaction will be ethylene glycol (EG) or methanol, depending on the type of reactant carbonate. Li and Wang [20] studied the main differences between using EC and DMC as reactants and found that when EC is used as the reactant, the reaction equilibrium

constant decreases with increasing temperature, while when DMC is used as the reactant, it is in contrast. For example, when using Al/Ca mixed oxide as the catalyst, the temperature adopted in the reaction between EG and glycerol is 35 °C [38], while to achieve the same GC conversion and selectivity, the temperature to be used in the reaction between DMC and glycerol should be higher than 80 °C [39]. In this way, it seems easier and more energy-efficient to synthesize GC by the reaction of EG and glycerol.

However, the separation process of the product should also be considered. From the physical properties of the compound, it is known that the boiling points of EC (261 °C) and EG (197 °C) are higher than the boiling points of DMC (90 °C) and methanol (64.5 °C). The separation of EC and EG requires more energy input. Therefore, from the perspective of energy saving, the advantages and disadvantages of the two reactions can offset each other [40].

5.1. Catalyst-Mediated Transesterification of EC with Glycerol

Ethylene carbonate is the simplest substance containing ODO groups, which can provide carbonate for the transesterification reaction. The reaction pathway is divided into the following two steps: the first step is to synthesize EC with titanium dioxide and ethylene oxide; the second step is through the transesterification of EC with glycerol to synthesize GC [41]. With EC as the reactant, the catalysts currently used in research include CaO, Al/Ca/Mg mixed oxides and hydrotalcite-like compounds, basic resins and molecular sieves, and also ionic liquids. The conversion rate after synthesis of GC is generally between 85–100%, the selectivity of GC is between 84–99% [41].

Climent et al. [40] selected hydrotalcite mixed metal oxides (Al/Mg and Al/Li) and alkaline oxides (MgO and CaO) as catalysts. The amount of catalyst was 0.5%, the reaction temperature was 35 °C, and finally a glycerol conversion of 98% was reached. They also showed that the strong alkaline Al/Ca-mixed oxide (AlCaMO) had the best catalytic activity. In the same year, Cho et al. [41] used ionic liquid as the catalyst, which was immobilized on the mesoporous material MCM41 (Mobil Composition of Matter No. 41, framework). The study showed that RNX-MCM41 with long alkyl chain had higher catalytic performance and its activity remained basically unchanged after it was used 3 times. Nevertheless, the method of synthesizing GC from glycerol and EC has the problem of not easily available raw materials, and the price is high. The by-product glycol produced in this reaction has a high boiling point making it difficult to separate from the product.

5.2. Catalyst-Mediated Transesterification of DMC with Glycerol

DMC is an environmentally friendly green chemical product, approved by European Union as a non-toxic substance that has become the most popular transesterification raw material in recent years. DMC is a solvent with a higher evaporation temperature and a faster evaporation rate. It has excellent solubility, can be used as a reactant and a solvent in the reaction system at the same time, no additional solvent is required. Not only does its reactivity meet the industry, but also its synthetic route is green and pollution-free [42][43]. However, the transesterification reaction of DMC with glycerol to afford GC is slow; hence, the catalyst plays a vital role in faster and selective production of GC. For this purpose, in recent years, the investigation of the reaction system of glycerol and DMC to synthesize GC, led to the search of different catalysts to be used in this reaction including

alkali and alkaline-earth metal catalysts, mixed oxide catalysts, biological enzyme catalysts and ionic liquid catalysts [\[44\]](#)[\[45\]](#)[\[46\]](#)[\[47\]](#)[\[48\]](#)[\[49\]](#).

5.3. The Future of the Transesterification Route

In view of the advantages and disadvantages of various types of catalysts, the best catalyst can be selected according to specific needs to suit the operating environment and economic conditions. For example, when considering economic benefits and production efficiency, you can choose the cheap alkaline-earth metal CaO, without considering its shortcomings of easy inactivation; when you need to obtain high purity and high value-added chemicals, you can choose high activity, stable but expensive catalysts, such as ILs, et cetera. At the same time, from the process point of view, the reactants are either not easy to obtain, or the synthesis cost is high, the process is complicated, and the reaction products are difficult to separate. Therefore, for the development of GC green synthesis, it is particularly important to seek a more optimized process for the reaction system.

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