

Research progress in the catalysts for direct carbonylation of glycerol with CO₂ to glycerol carbonate

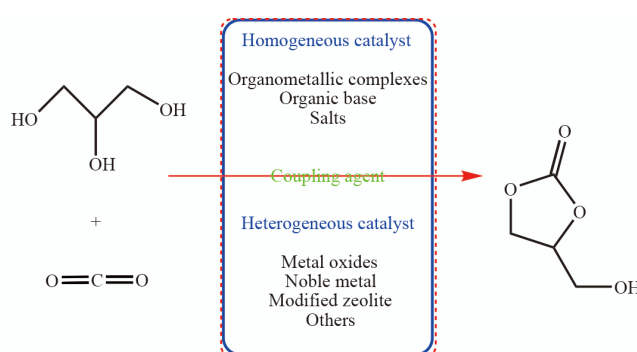
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Abstract: The carbonylation of glycerol with carbon dioxide (CO₂) to produce glycerol carbonate is an effective route for the resource utilization of CO₂, which can not only alleviate the carbon emission but also enable the synthesis of value-added chemicals. As this reaction process suffers from low glycerol conversion due to the thermodynamic limitation, introducing a coupling agent besides an appropriate catalyst is necessary to achieve the efficient synthesis of glycerol carbonate. This article systematically reviews the recent research progress in the



homogeneous catalysts (inorganic bases and organic bases) and heterogeneous catalysts (Zn, Cu, Ce, La, Mg, noble metal, modified zeolite, non-metallic materials, etc.) for the direct carbonylation of glycerol with CO₂. The strategies such as metal oxide modification, support optimization, precursor selection, and construction of acidic-basic sites to enhance the catalytic performance are analyzed, while the effects of coupling agents (acetonitrile, adiponitrile, 2-cyanopyridine, MgCO₃, CaC₂, NaHCO₃, etc.) are summarized. Among them, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), Zn(NTf)₂, and metal composite oxides such as ZnO-CeO₂ have demonstrated promising catalytic performance in the carbonylation of glycerol with CO₂. To enhance the efficiency for the carbonylation of glycerol with CO₂, following measures should be taken in the future: developing organometallic complexes or composite metal oxides with highly dispersed active sites and specially tailored morphologies to modulate the surface area, pore size, and surface acidity/basicity of the catalysts; optimizing coupling agents or designing novel membrane reactors to improve the glycerol conversion; introducing polar solvents to improve the adsorption and activation capabilities of reactants and thereby to boost the catalytic activity. All these would provide valuable references for the catalyst design and reaction system optimization in the carbonylation of glycerol with CO₂.

Key words: CO₂; glycerol; carbonylation; glycerol carbonate; catalysts

Since the Industrial Revolution, the extensive utilization of fossil fuels such as coal, oil, and natural gas has led to a sharp increase in the emission of CO₂ to atmosphere, contributing to the greenhouse effect and causing significant damage to the global ecological environment. In 2016, numerous countries around the world reached the Paris Agreement, aiming to address the rise in global average temperatures. China announced its “dual-carbon” goals in 2020: peaking carbon emissions before 2030 and achieving

carbon neutrality before 2060. The conversion of CO₂ into high-value products such as chemicals, fuels, and materials through catalytic processes is regarded as a critical pathway to achieving carbon neutrality, which contributes to building a green and sustainable carbon cycle system.

Biodiesel (fatty acid methyl esters, FAMES), known for its advantages such as renewability, low combustion emissions, and high biodegradability, has experienced rapid development. Biodiesel is typically produced through the

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transesterification and esterification of animal or vegetable oils with light alcohols. Generally, for every 1.0 kg of biodiesel produced, approximately 0.1 kg of crude glycerol is generated^[1-2]. That is, the growing biodiesel industry generates a substantial amount of glycerol as by-product. From 2023 to 2025, the biodiesel market is projected to reach 73.39 million tons per year, and annual glycerol production is expected to reach around 11.5 million tons by 2025^[3]. The utilization of glycerol has become a bottleneck affecting the sustainable development of the biodiesel industry.

Currently, high-value chemicals produced from glycerol as a raw material primarily include: propylene glycol, acrolein, propionic acid, glycerol carbonate (GC), epichlorohydrin, dihydroxyacetone, glyceric acid, multi-branched polymers and so on^[2,4-5]. Among them, glycerol carbonate exhibits properties such as high boiling point (350 °C at 760 mmHg), high flash point (110 °C, open cup method), and low volatility (vapor pressure of 800 Pa at 177 °C). It can serve as a versatile, low-volatility organic solvent and finds applications in gas separation, battery electrolytes, lubricants, cosmetics and so on^[6-8]. Additionally, glycerol carbonate contains a highly reactive five-membered cyclic carbonate ring and a hydroxyl functional group, enabling it to undergo nucleophilic and electrophilic reactions for the synthesis of other new compounds^[7]. Therefore, the production of glycerol carbonate from glycerol holds significant importance.

At present, the main methods reported in the literature for synthesizing glycerol carbonate from glycerol include: transesterification, glycerol + urea, glycerol + CO, glycerol + phosgene, glycerol + CO₂, etc.^[9-10], as illustrated in Figure 1. The glycerol + phosgene method has the advantages of good reaction activity and high product yield, but needs an extremely low operation temperature (−70 °C); the significant drawback of this process is its low atomic economy and using highly toxic and corrosive phosgene, which have been banned in some countries for safety reasons^[11]. The reaction between glycerol and urea not only produces glycerol carbonate but also generates harmful isocyanic acid and dicyandiamide as by-products; moreover, the entire reaction process must be carried out under vacuum conditions to remove the generated ammonia^[12] and the operation under negative pressure results in a significant increase in the equipment investment costs. Glycerol and organic carbonates (such as dimethyl carbonate, ethylene carbonate, and propylene carbonate) react through transesterification to produce glycerol carbonates, which displays high reaction activity under mild conditions; however, the cost of the raw material organic carbonates is relatively high^[13]. Moreover, the reaction is reversible, and usually requires an excess of glycerol to shift the equilibrium, thus resulting in high energy consumption for product separation and poor overall economic.

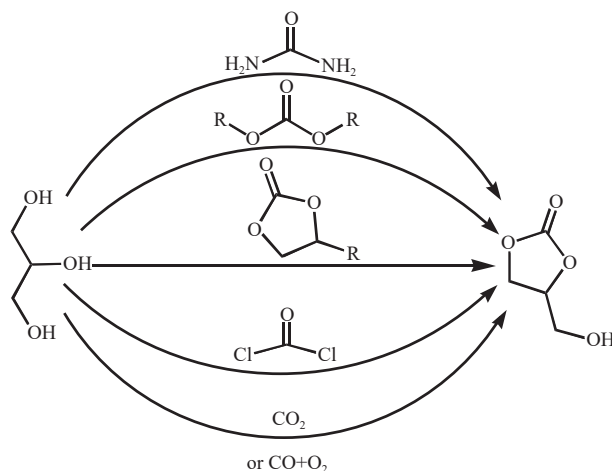
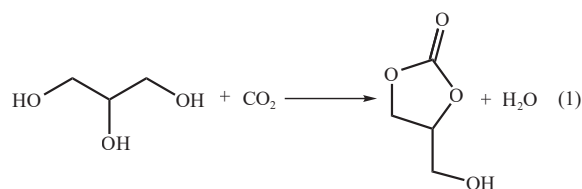


Fig. 1 Main methods for preparing glycerol carbonate from glycerol

Compared with other synthetic methods, the reaction of glycerol with CO₂ to produce glycerol carbonate is a green synthetic route (Equation (1)). On the one hand, it can utilize the cheap CO₂ as a carbonylation reagent, which is helpful in addressing the carbon emission issue under the “dual-carbon” target; on the other hand, it can also solve the problem of converting glycerol into value-added products. Moreover, the atomic utilization rate of this route reaches 86.8%, with water as the only by-product. It is currently the most environmentally friendly and economically viable synthetic method, thus attracting the attention of many scholars. Zhao et al.^[14] calculated the enthalpy changes, Gibbs free energy changes and standard equilibrium constants involved in this reaction using the Benson group contribution method, the Joback group contribution method and the Sterlning-Brown equation. Within the temperature range of 298 to 518 K, the Gibbs free energy of this reaction was always greater than zero, indicating that the reaction was thermodynamically unfavorable. By introducing coupling agent and designing a coupled reaction to remove the by-product water generated during the reaction process, the Gibbs free energy of the reaction could be significantly reduced, thereby breaking the thermodynamic limitation. In addition, this route requires the development of efficient catalysts to accelerate its industrialization process.



At present, the research on this method mainly focuses on the selection of efficient catalysts, coupling agents, and reaction solvents. This paper reviews the research progress of homogeneous catalysts and heterogeneous catalysts for the carbonylation of glycerol with CO₂ in recent years, analyzes the relationship between the structures, physical properties and activity of various catalysts, and summarizes

the reaction mechanisms.

1 Progress in catalyst research

Vieville and coworkers^[15] may be the first ones who proposed the synthesis of glycerol carbonate through the reaction of CO₂ with glycerol. Under supercritical CO₂, good reaction results were achieved by using ion exchange resins and molecular sieves as catalysts. However, when ethylene carbonate was introduced as the solvent in the reaction system, transesterification reaction was triggered. Therefore, strictly speaking, in their synthetic route, CO₂ was not directly used as the carbonylation reagent. Later, Aresta et al. used organic tin as the catalyst and pioneered the direct carbonylation of CO₂ to prepare glycerol carbonate^[16]. The results showed that glycerol carbonate can be obtained on both homogeneous catalysts and heterogeneous catalysts. Generally speaking, homogeneous catalysts display adequate conversion of raw materials and selectivity to products under mild conditions; however, they also face problems of catalyst separation and reuse. Therefore, recent research has shifted towards using heterogeneous catalysts, especially metal oxide solid base

catalysts. Coupling agents such as adiponitrile, acetonitrile, CaC₂, MgCO₃ and 2-cyanopyridine were also used in the research to eliminate water and promote the shift of the reaction equilibrium towards the carbonate product. This article will conduct a comprehensive summary of the research on homogeneous and heterogeneous catalysts in recent years, with the aim of providing reference for the development of efficient catalysts.

1.1 Homogeneous catalyst

Table 1 gives the commonly seen homogeneous catalysts for the glycerol carbonylation with CO₂. Aresta, George and co-workers^[16–17] investigated the activity of Sn-based catalysts (*n*-Bu₂Sn(OMe)₂, *n*-Bu₂SnO and Sn(OMe)₂) for the synthesis of glycerol carbonate. They found that in the presence of methanol, *n*-Bu₂SnO first reacted with methanol to form *n*-Bu₂Sn(OMe)₂ with better catalytic activity, and then participated in the reaction of CO₂ with glycerol. As demonstrated in Figure 2, glycerol first forms a cyclic Sn-glycerol complex with *n*-Bu₂Sn(OMe)₂, and then CO₂ inserts into the complex, undergoing intramolecular rearrangement to form the glycerol carbonate product.

Table 1 Homogeneous catalysts for the glycerol carbonylation

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
<i>n</i> -Bu ₂ Sn(OMe) ₂	180 °C, 5 MPa-CO ₂ , 15 h	–	6.86	–	[16]
<i>n</i> -Bu ₂ SnO+13X	120 °C, 13.8 MPa-CO ₂ , 4 h	–/MeOH	–	35	[17]
Cs ₂ CO ₃	175 °C, 8.0 MPa-CO ₂ , 12 h	acetonitrile	16.8	10.5	[18]
TBD	175 °C, 8.0 MPa-CO ₂ , 12 h	acetonitrile	20.5	12.4	
DBU	70 °C, 1 MPa-CO ₂ , 18 h	CH ₂ Br ₂ /bmimPF ₆	–	86	[19]
TBD	155 °C, 4.5 MPa-CO ₂ , 16 h	acetonitrile	59	20	[20]
DBU	155 °C, 4.5 MPa-CO ₂ , 16 h	acetonitrile	57	22	
Cobalt acetate	180 °C, 2 MPa-CO ₂ , 6 h	acetonitrile	36.7	4.6	[21]
2-Cyanopyridine	180 °C, 15 MPa-CO ₂ , 12 h	–	46.5	18.7	[22]
Zn(OTf) ₂	180 °C, 5 MPa-CO ₂ , 24 h	CaC ₂ /1-methyl-2-pyrrolidone	–	92	[23]
Zn(OTf) ₂ /1, 10-phenanthroline	170 °C, 5 MPa-CO ₂ , 48 h	CaO/N-methyl-2-pyrrolidone	–	80	[24]

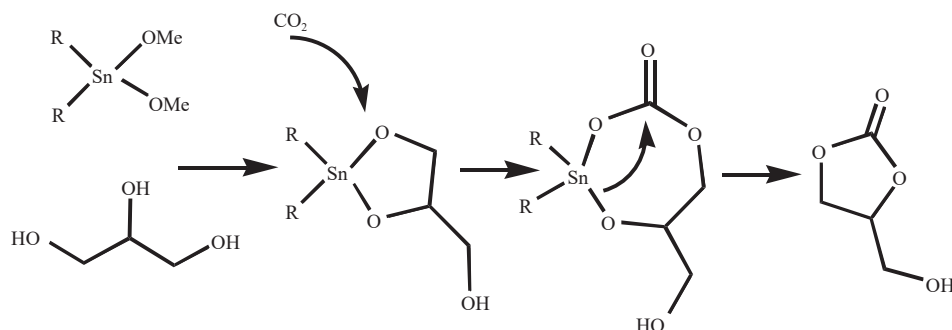


Fig. 2 Mechanism for the synthesis of glycerol carbonate from glycerol and CO₂ over *n*-Bu₂Sn(OMe)₂

Huang et al.^[18] conducted the glycerol carbonylation reaction with CO₂ by using acetonitrile as the solvent on both inorganic and organic base catalysts, where the inorganic base catalysts covered Cs₂CO₃, CsOH, K₂CO₃, KOH, Na₂CO₃, NaOH, KCl, KBr, KF, KI, K₃PO₄, K₂SO₄, KNO₃ and the organic base catalysts included 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine ((Et)₃N) and diethylamine ((Et)₂NH). The results indicated that the catalytic activity was somewhat related to the basicity strength, with Cs₂CO₃ and TBD showing highest activity among the catalysts tested. Acetonitrile not only acts as a solvent during the reaction process, but also functions as a dehydration agent, significantly increasing the conversion of glycerol and the yield of glycerol carbonate. Using Cs₂CO₃ as the catalyst, under the conditions of 8 MPa and 175 °C for 12 h, the conversion of glycerol was 16.8% and the selectivity of glycerol carbonate was 62.5%; using TBD as the catalyst, in contrast, the conversion of glycerol was 20.5% and the selectivity of glycerol carbonate was 60.3%.

Using the organic base DBU as the catalyst, Lim et al.^[19] introduced the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) to increase the solubility of CO₂. At the same time, CH₂Br₂ was used as the activator for the polyol, which could significantly enhance the reaction activity, achieving a glycerol carbonate yield of 86%.

Moreover, such a reaction system also performed well for the direct synthesis of carbonates from CO₂ and other alcohols. Furthermore, Chibane et al.^[20] used acetonitrile as the coupling agent; under the optimal conditions, with TBD and DBU as the catalysts, the yields of glycerol carbonate were 20% and 22%, respectively. The DFT calculation results indicated that the catalyst reduced the reaction energy barriers of different steps and the intramolecular ring closure was the rate-limiting step; it was believed that the acetonitrile hydrolysis reaction had a high energy barrier and was of low efficiency as the coupling agent.

In addition, it was found that cobalt acetate (Co(OAc)₂) was better than other acetates like Mn(OAc)₂, K(OAc), Zn(OAc)₂, Pb(OAc)₂ and Ca(OAc)₂ in synthesizing glycerol carbonate from glycerol and CO₂^[21]; under the optimal reaction conditions, the glycerol conversion was 36.7%, but the selectivity to glycerol carbonate was only 12.5%.

Su et al.^[22] discovered that 2-cyanopyridine not only served as a catalyst but also acted as a coupling agent to facilitate the reaction progress, owing to the strong ability of 2-cyanopyridine in the CO₂ adsorption and activation. 2-Cyanopyridine can form a five-membered ring by combining with CO₂ through conjugated nitrogen, activating CO₂ and then reacting with glycerol to produce glycerol carbonate, as illustrated in Figure 3.

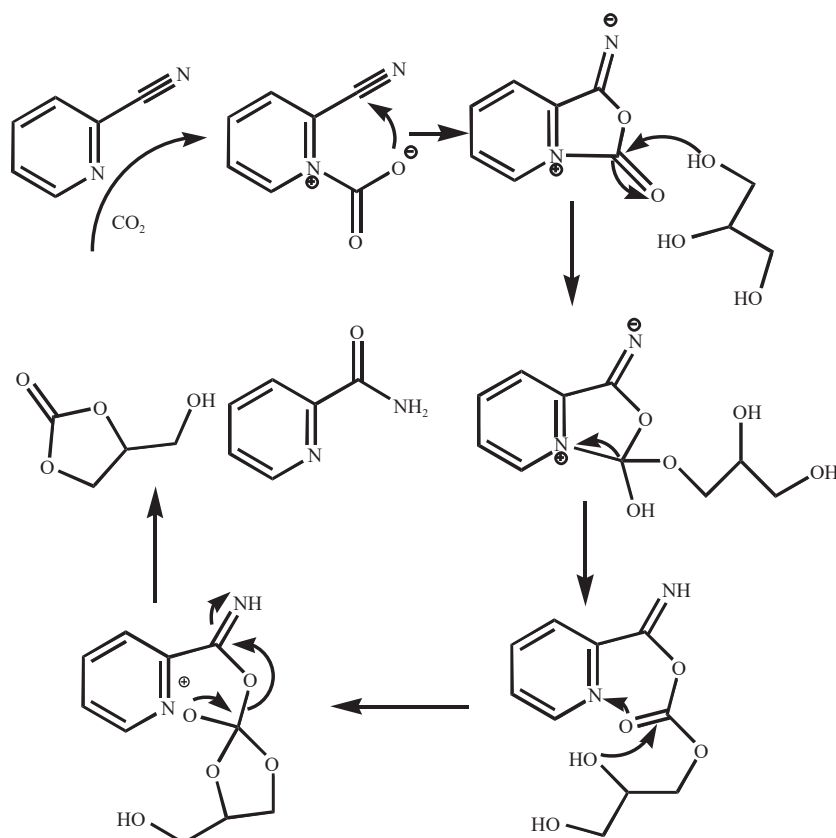


Fig. 3 Possible mechanism of glycerol carbonylation by using 2-cyanopyridine

Zhang et al.^[23] observed that the coordination of $\text{Zn}(\text{OAc})_2$, ZnSO_4 , ZnCl_2 , ZnBr_2 , ZnI_2 and $\text{Zn}(\text{OTf})_2$ with 1,10-phenanthroline could form effective complex catalysts. Under the conditions employing 1-methyl-2-pyrrolidone as the solvent and CaC_2 as the coupling agent, all catalysts exhibited good activity. When $\text{Zn}(\text{OTf})_2$ was used as the catalyst, a glycerol carbonate yield of 92% was achieved, which was mainly attributed to the strong Lewis acidity of $\text{Zn}(\text{OTf})_2$. The ligand also played a decisive role, as the yield decreased to 37% in the absence of the ligand. Furthermore, they investigated the influence of reaction solvents (*N*, *N*-dimethylformamide, dimethylacetamide, methyl ethyl ketone, tetrahydrofuran, toluene) on the catalytic activity and found that higher solvent polarity led to greater reaction activity. Additionally, using $\text{Zn}(\text{OTf})_2/1,10\text{-phenanthroline}$ as the catalyst, they examined the effects of different dehydrating agents (4A molecular sieve, K_2CO_3 , CaSO_4 , MgO , CaO) on the reaction and found that CaO performed the best. Under the optimal reaction conditions, the yield of glycerol carbonate reached approximately 80%^[24]. This catalytic system also demonstrated good performance in the synthesis of other cyclic carbonates from polyols and CO_2 .

Homogeneous catalysts primarily consist of metal-organic complexes and organic bases, which generally require coupling agents to achieve good catalytic performance. Using acetonitrile as a coupling agent may generate certain by-products, resulting in lower selectivity to the target product. In contrast, employing inorganic dehydrating agents (such as CaC_2 or CaO) in combination with solvents that can promote the activation of glycerol or CO_2 , such as *N*-methyl-2-pyrrolidone or bmimPF_6 , can significantly enhance both reaction activity and selectivity toward the target product. However, due to challenges such as difficulty in separation and deactivation of homogeneous catalysts, the research on homogeneous catalysts has been relatively limited in recent years. Future work could use homogeneous catalysts as model systems to gain deeper insights into the fundamental effects of coupling agents and reaction solvents, and establish reaction mechanisms through theoretical calculations, thereby providing guidance for the development of efficient heterogeneous catalysts and reaction systems.

1.2 Heterogeneous catalyst

Compared to the homogeneous catalysts, the heterogeneous catalysts, while offering easier separation, often exhibit lower catalytic activity. Metal oxides such as ZnO , CuO , CeO_2 , La_2O_3 and MgO have demonstrated certain catalytic activities. The structure-activity relationships of these metal oxides were investigated through methods like structural optimization and the preparation of composite metal oxides and the effects of coupling agents and solvents on reaction performance were analyzed. Additionally, some noble metal catalysts, modified zeolites, and other non-metallic catalysts have also been developed. In contrast to traditional thermal catalysis, photocatalysis utilizes light energy to drive the reactions

and can significantly reduce energy consumption. Accordingly, researchers have also innovatively proposed the photothermal synergistic catalysis, pioneering a new approach for the synthesis of glycerol carbonate.

1.2.1 Zn-based catalyst

Table 2 gives the commonly seen Zn- and Cu-based oxide catalysts for the glycerol carbonylation with CO_2 . Mota et al. prepared ZnO , SnO_2 , Fe_2O_3 , CeO_2 and La_2O_3 via the sol-gel method using polyvinyl alcohol as a template^[25]; they found that ZnO exhibited relatively high catalytic activity and the used ZnO could maintain favorable catalytic performance even after calcination at 450 °C.

The introduction of other metals to form composite metal oxides can modulate the surface alkalinity of ZnO , which facilitates the adsorption and activation of CO_2 and enhances the reaction activity. Li et al.^[26] prepared a series of Zn-La composite oxide catalysts with different Zn/La ratios via the co-precipitation method and investigated the effect of calcination temperature on the structural properties of the catalysts. The results indicated that when calcined at 500 °C, La mainly existed in the form of $\text{La}_2\text{O}_2\text{CO}_3$. The formation of $\text{La}_2\text{O}_2\text{CO}_3$ species helps to improve the surface alkalinity of the catalyst, thereby promoting the adsorption and activation of CO_2 and facilitating the reaction. Furthermore, Park et al.^[27] prepared the $\text{ZnO-La}_2\text{O}_2\text{CO}_3$ composite oxide catalysts with different morphologies via co-precipitation and glycol combustion methods, and investigated the effects of oxide ratio and crystal structure on the catalytic performance. The results showed that the catalyst synthesized by the glycol combustion method exhibited superior product selectivity, which was mainly attributed to the monoclinic crystal structure of $\text{La}_2\text{O}_2\text{CO}_3$. After the reaction, the catalyst prepared by co-precipitation showed significant accumulation of zinc glycerolate intermediates on its surface, while the material prepared by glycol combustion only had a small amount of zinc glycerolate. This difference is primarily due to the fact that the monoclinic $\text{La}_2\text{O}_2\text{CO}_3$ facilitates the reaction between zinc glycerolate and CO_2 to form glycerol carbonate, thereby enhancing the selectivity toward glycerol carbonate.

Liu et al.^[28] prepared a series of $\text{ZnWO}_4\text{-ZnO}$ catalysts with different tungsten loadings using the impregnation method and evaluated their activity using *N*, *N*-dimethylformamide as the reaction solvent. Under optimal reaction conditions, the glycerol carbonate yield reached 6.5% with 100% selectivity on the 10%W-Zn catalyst. The catalytic performance of the Zn-W composite oxide catalysts was attributed to the formation of ZnWO_4 , the interaction between ZnWO_4 and ZnO , the moderate acid-base sites, and the specific surface area of the catalysts. DRIFTS results indicated that on the ZnO surface, CO_2 primarily existed in the form of chelating bidentate carbonates, whereas after the introduction of W, bridged bidentate carbonates became the dominant adsorption form of CO_2 . Infrared spectroscopic characterization of the catalyst after the reaction revealed the formation of zinc glycerolate species, based on which a possible reaction

mechanism was proposed, as shown in Figure 4.

To further increase the specific surface area of the catalysts and expose more active sites, Li et al.^[29–30] prepared a series of Zn-Al-La catalysts derived from hydrotalcite precursors, as well as cation-modified (Li, Mg, Zr) and anion-modified (F, Cl, Br) Zn-Al-La catalysts. Under the condition of using acetonitrile as the coupling agent, favorable results were achieved. *In situ* infrared

spectroscopy results indicated that ZnO on the catalyst surface activated glycerol to form zinc glycerolate. The activated CO₂ on basic sites was then inserted into zinc glycerolate, generating a seven-membered ring intermediate species, which subsequently underwent intramolecular rearrangement to form the target product, glycerol carbonate (GC). The detailed mechanism is illustrated in Figure 5.

Table 2 Zn- and Cu-based oxide catalysts for the glycerol carbonylation

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
ZnO	180 °C, 15 MPa-CO ₂ , 12 h	—	—	8.1	[25]
ZnO-La ₂ O ₂ CO ₃	170 °C, 4.0 MPa-CO ₂ , 12 h	acetonitrile	30.3	14.3	[26]
ZnO-La ₂ O ₂ CO ₃	170 °C, 4.0 MPa-CO ₂ , 12 h	acetonitrile	24.3	14.1	[27]
ZnWO ₄ -ZnO	150 °C, 5 MPa-CO ₂ , 6 h	—/ <i>N,N</i> -dimethylformamide	6.5	6.5	[28]
Zn/Al/La-Li	170 °C, 4.0 MPa-CO ₂ , 12 h	acetonitrile	35.7	15.1	[29]
Zn/Al/La-Cl	170 °C, 4.0 MPa-CO ₂ , 12 h	acetonitrile	35.5	16.0	[30]
ZnAlCe	170 °C, 4.5 MPa-CO ₂ , 12 h	acetonitrile	56.7	28.9	[31]
La ₂ O ₂ CO ₃ -ZnO	150 °C, 5.5 MPa-CO ₂ , 6 h synergistic photocatalysis	—/ <i>N,N</i> -dimethylformamide	6.9	6.1	[32]
Co ₃ O ₄ -ZnO	150 °C, 5 MPa-CO ₂ , 6 h synergistic photocatalysis	—/ <i>N,N</i> -dimethylformamide	6.0	5.3	[33]
CuO	120 °C, 3 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	89	61.7	[34]
Cu/La ₂ O ₃	150 °C, 7.0 MPa-CO ₂ , 12 h	acetonitrile	33.4	15.1	[35]
CuO/Al ₂ O ₃	150 °C, 4.0 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	41.3	17.5	[36]
CuO/CeO ₂ /ZnO	160 °C, 6.0 MPa-CO ₂ , 6 h	acetonitrile	57.4	57.2	[37]
CuO/In ₂ O ₃ -ZnO	150 °C, 5 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	38	24.46	[38]

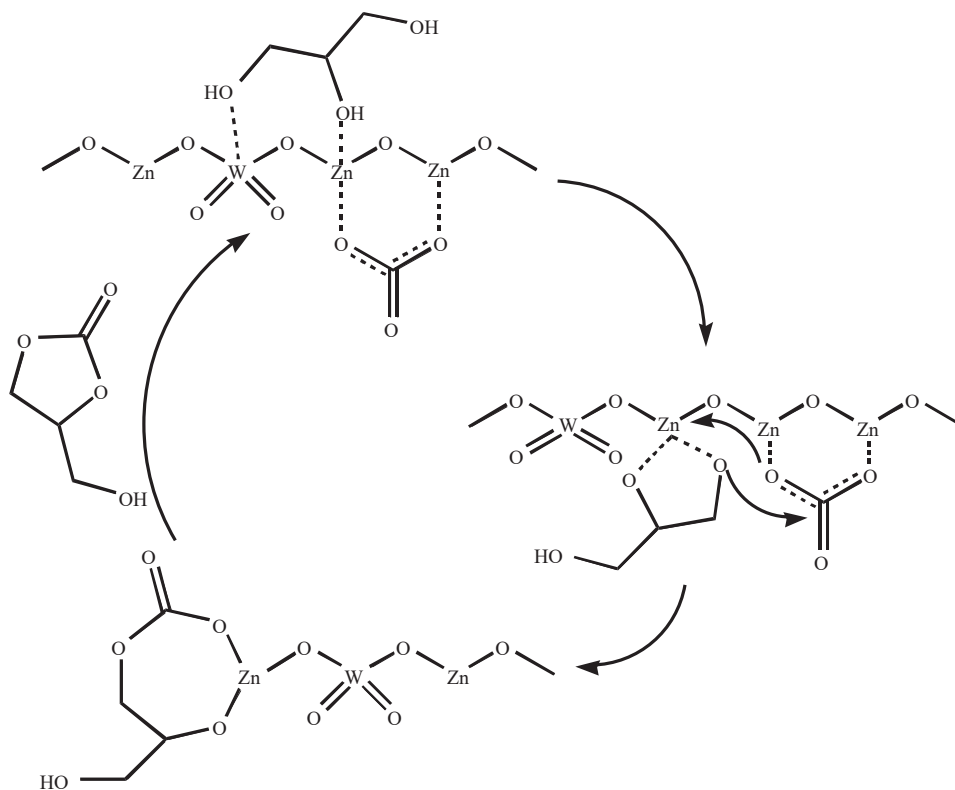


Fig. 4 Possible mechanism for the synthesis of glycerol carbonate from glycerol and CO₂ over ZnWO₄-ZnO

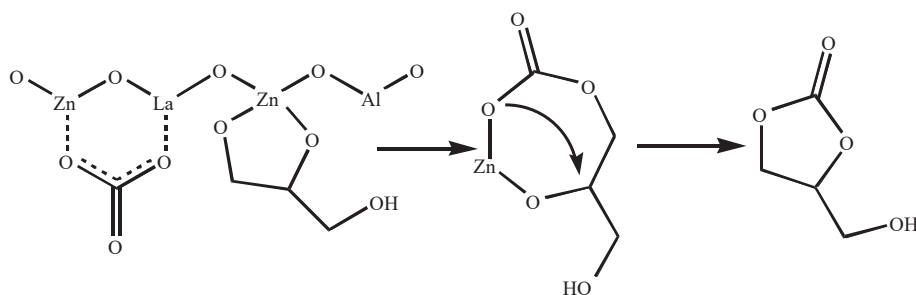


Fig. 5 Reaction mechanism for the synthesis of glycerol carbonate over Zn-La catalysts

Furthermore, Cao et al.^[31] synthesized the ZnAlCe composite metal oxide catalysts *via* the co-precipitation method. Compared with pure ZnO, the introduction of Al increased the specific surface area of the catalyst, thereby exposing more active sites. The XPS results revealed that Zn in the Zn₄AlCe catalyst promoted the conversion of Ce⁴⁺ to Ce³⁺ in CeO₂. The incorporation of CeO₂ significantly enhanced the lattice oxygen content of the catalyst and the lattice oxygen, acting as a Lewis base site, facilitates the activation of CO₂. The solid Zn₄AlCe_x catalyst possesses abundant acid-base sites, which are spatially constrained and unable to freely combine, forming frustrated Lewis pairs (FLPs). The activity test results indicated that the ZnAlCe composite oxide catalyst exhibited favorable performance, primarily due to the introduction of Ce, which helped to increase the lattice oxygen on the catalyst surface and form a higher number of FLPs, thereby promoting the reaction. As the Ce content increased, the number of FLPs decreased, leading to a decrease in the catalytic activity. The FT-IR results showed that CO₂ was mainly adsorbed and activated on the material surface in the form of monodentate and bidentate carbonates and the introduction of Ce could enhance the adsorption intensity. Additionally, the formation of the intermediate species zinc glycerolate was observed.

Compared with the thermal catalysis, Li et al.^[32] conducted a study on the photothermal catalytic synthesis of glycerol carbonate using ZnO-La₂O₃CO₃ under light irradiation. The results showed that the introduction of La enhanced the number of basic sites on the catalyst surface, which contributed to the thermal catalytic reaction. Simultaneously, the incorporation of La also improved the light absorption capacity of the catalyst, promoting the generation of electron-hole pairs. The electrons facilitated the activation of CO₂, while the holes promoted the activation of glycerol, thereby enhancing the overall reaction performance. The photothermal synergistic effect significantly improved the catalytic performance, nearly doubling the yield of glycerol carbonate. Furthermore, they prepared a ZnO-Co₃O₄ catalyst. Under photothermal synergistic conditions, the introduction of Co enhanced the surface basicity (both strength and quantity) of the catalyst. The synergistic interaction between ZnO and Co₃O₄ reduced the bandgap of Co₃O₄-ZnO and improved its visible-light absorption capacity, enabling the catalyst to generate electron-hole pairs through visible light excitation^[33]. The

photothermal synergy contributed to increased reaction activity, while the strong visible-light harvesting ability and efficient electron-hole separation achieved by incorporating Co enhanced the reactivity under visible light irradiation.

Zinc-based bimetallic composite metal oxides such as ZnO-La₂O₃CO₃, Co₃O₄-ZnO, ZnWO₄-ZnO, as well as trimetallic composite oxides like ZnAlLa and ZnAlCe, have all shown certain effectiveness in this reaction. The increase in catalyst specific surface area, oxygen vacancies and the number of Lewis acid-base sites contributes to the enhanced reaction performance. Using *N,N*-dimethylformamide as a solvent promotes the adsorption and activation of CO₂, facilitating the reaction. Employing acetonitrile as a coupling agent significantly improves the conversion of glycerol, albeit with lower selectivity toward glycerol carbonate. The formation of the intermediate species zinc glycerolate has been observed in all Zn-based catalytic systems. CO₂ predominantly exists in a bidentate carbonate adsorption form on the catalyst surface, which aligns with the reaction mechanisms proposed by other researchers (Figures 4 and 5). Photothermal synergy markedly enhances the performance of the catalytic reaction. Zn-based catalysts represent one of the earlier studied metal oxide catalysts. Through approaches such as metal modification, morphology control to increase the specific surface area, and photothermal synergy, the reaction activity has been significantly improved. However, the highest yield of glycerol carbonate achieved so far remains only 28%, indicating that further optimization of Zn-based catalysts is still required to enhance their activity. In future catalyst design, consideration could be given to preparing composite metal oxides with specific structures such as perovskite or spinel, aiming to further increase the specific surface area and modulate the surface acidity and alkalinity. Alternatively, exploring other coupling agents or combinations of reaction solvents and coupling agents may help improve the reaction activity.

1.2.2 Cu-based catalyst

Ke et al.^[34] prepared metal oxides such as CuO, NiO, Co₃O₄, ZrO₂ and Al₂O₃ *via* the hydrothermal method. Among them, CuO exhibited a porous flake-like stacked structure with relatively small specific surface area, pore size and pore volume. Lattice oxygen contributes to the activation of glycerol, while oxygen vacancies facilitate the

adsorption and activation of CO₂. The CuO material showed a higher number of lattice oxygen and oxygen vacancies, with their proportions close to 1:1. Furthermore, CuO and Co₃O₄ possessed few acidic sites on their surfaces, as strong acidic sites tend to cause aggregation of active components on the catalyst surface, thereby reducing catalytic activity. The CO₂-TPD results indicated that CuO had a higher proportion of strong basic sites compared to other metal oxides, which aids in the activation of glycerol. Consequently, CuO demonstrated superior catalytic activity relative to other oxide catalysts and could be reused for multiple cycles. Under optimal reaction conditions, the glycerol conversion reached 89%, with a glycerol carbonate yield of 61.7%.

To further enhance the dispersion and catalytic activity of Cu, a series of supported catalysts were prepared using the impregnation method. Zhang et al.^[35] synthesized Cu/La₂O₃ catalysts with different Cu loadings and reduced the active Cu component under a hydrogen atmosphere, investigating the effects of reaction conditions on the catalytic performance. The results demonstrated that Cu and La₂O₃ synergistically promoted the activation of CO₂ and glycerol and the 2.3% Cu/La₂O₃ catalyst exhibited the best performance. There was a certain correlation between the size effect of Cu nanoparticles and their activity: as the Cu particle size increased from 1.7 to 11.9 nm, the turnover frequency decreased from 0.0096 to 0.0001 s⁻¹. Additionally, for the catalysts such as Cu/CaO, Cu/MgO, Cu/La₂O₃, Cu/Al₂O₃, Cu/ZrO₂, Cu/Mg-Al-Zr, Cu/CNTs, Cu/MCM-41 and Cu/HZSM-5 prepared *via* impregnation^[39], the distribution and particle size of Cu on the carriers varied due to differences in the interaction between Cu and the supports, as did the number of acid-base sites on the support surfaces. The results indicated that both Cu particle size and the acid-base properties of the catalyst influenced the conversion of glycerol to glycerol carbonate and glyceryl monoacetate. As the Cu particle size increased, the reaction rate of glycerol decreased. Moreover, the catalysts containing Lewis basic sites favored the formation of glycerol carbonate, whereas those containing Lewis acidic sites promoted the formation of glyceryl monoacetate.

Al-Kurdhani et al.^[36] prepared the Cu catalysts supported on different carriers (graphene oxide, graphene, activated carbon, SiO₂, Al₂O₃) using the impregnation method, among which the Al₂O₃-supported catalyst exhibited the best activity. The studies on the effects of Cu loading and calcination temperature showed that the optimal catalytic performance was achieved with a Cu loading of 30% and a calcination temperature of 700 °C. This is primarily attributed to the fact that the catalyst calcined at 700 °C demonstrated the largest specific surface area and total pore volume, which likely led to greater exposure of active sites and consequently higher activity. Additionally, increasing the calcination temperature facilitated the formation of CuAl₂O₄, resulting in an increased number of moderate to

strong basic sites on the catalyst surface, which promoted the activation of glycerol and CO₂, thereby enhancing the activity. They also proposed a possible reaction mechanism (Figure 6): First, the O–H bond of glycerol is adsorbed and activated by the strong basic sites of the CuO/Al₂O₃ catalyst. Subsequently, the second O–H bond of the glycerol molecule is also activated, forming Cu(C₃O₃H₆), while the CO₂ molecule interacts with 2-cyanopyridine to form a five-membered ring intermediate (I). Next, the activated glycerol molecule undergoes nucleophilic attack on the carbonyl carbon atom of the intermediate, forming intermediate (II). Finally, the oxygen atom from the second O–H bond of glycerol performs an intramolecular nucleophilic attack on the carbonyl carbon, yielding glycerol carbonate.

Pawar et al.^[37] found that single metal oxides such as ZnO, CuO, CeO₂ and ZrO₂ exhibited certain catalytic activity for this reaction. Subsequently, bimetallic oxide catalysts CuO/ZnO and CeO₂/ZnO were prepared, and their activity was significantly enhanced compared to the single metal oxides. Following this, a trimetallic oxide catalyst CuO/CeO₂/ZnO was synthesized, and the loadings of Ce and Cu were optimized. The effects of reaction temperature, time, pressure, and catalyst dosage on the activity were investigated and the results showed that under 160 °C, 6 MPa CO₂, and a catalyst dosage of 10% for 6 h, the yield of glycerol carbonate reached 57.2% with nearly 100% selectivity to carbonate. Moreover, the catalyst could be reused for multiple cycles.

Sarkar et al.^[38] prepared In₂O₃-ZnO composite metal oxides *via* the precipitation method, followed by the synthesis of CuO/In₂O₃-ZnO catalysts with different Cu loadings using the impregnation method. As the Cu content increased, the catalyst pore size gradually expanded and the number of acid-base sites on the surface also increased. The Cu sites played a crucial role in the activation of CO₂ molecules, and the synergistic interaction between Cu and Lewis bases (In₂O₃/ZnO) activated CO₂, enabling its insertion into the bond between Cu and the Lewis base to form a Cu-O-CO-(In₂O₃/ZnO) complex. The generated bridged bidentate carbonate facilitated the progression of the reaction. Among various catalysts, 2% Cu/In₂O₃/ZnO exhibited the best catalytic activity. Under optimal conditions, the glycerol conversion reached 38%, and the glycerol carbonate yield was 24.46%.

The aforementioned Cu-based catalysts, primarily including CuO, bimetallic oxides (Cu/La₂O₃, CuO/Al₂O₃), and trimetallic composite oxides (CuO/CeO₂/ZnO, CuO/In₂O₃-ZnO), have been applied to this reaction. The effects of coupling agents such as acetonitrile and 2-cyanopyridine on the reaction were also investigated. The results indicate that many factors such as the number of strong basic sites, specific surface area, and pore size in CuO materials significantly influence the reaction activity. Furthermore, the use of suitable reaction solvents helps to enhance the catalytic performance.

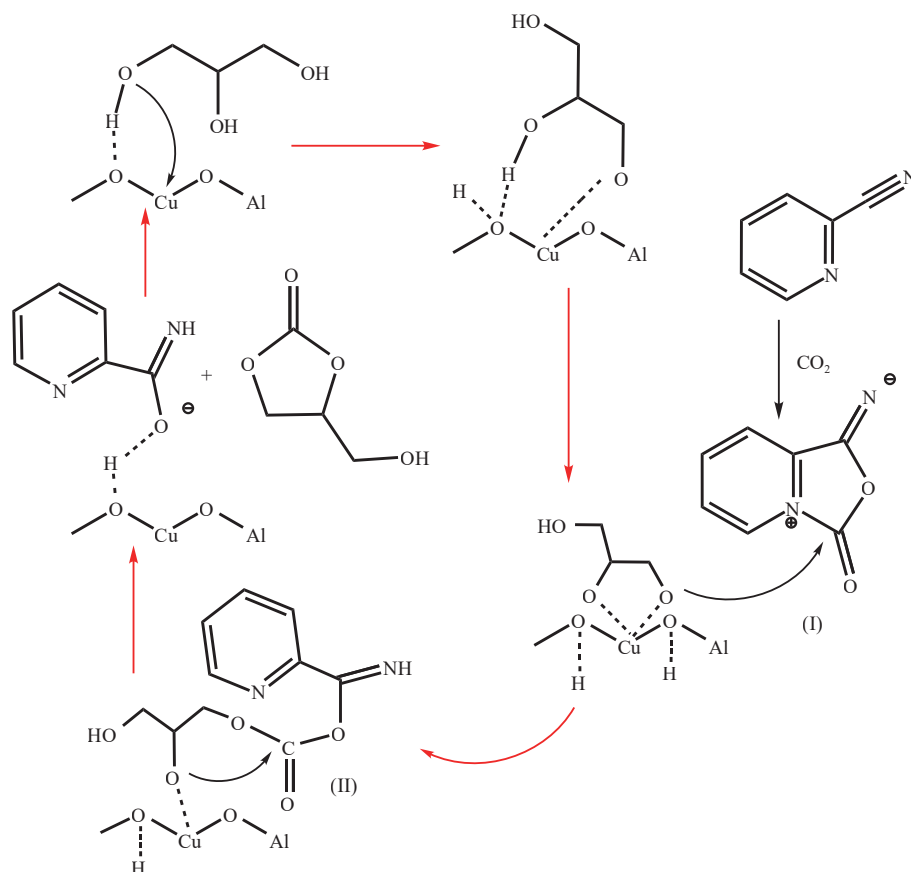


Fig. 6 Possible mechanism for the synthesis of glycerol carbonate over Cu-based catalysts

Additionally, for the Cu-supported catalysts, a correlation exists between Cu particle size and catalytic activity. The reaction mechanism over the Cu-based catalysts is similar to that over the Zn-based catalysts, involving the intermediate species of copper glycerolate. Although the impregnation method improves the dispersion of Cu and the introduction of other metals modifies the surface acidity and alkalinity of the material, the catalytic activity has not been significantly enhanced. In the future, in-depth research into the mechanism of Cu-based catalysts is needed to enable targeted adjustments of the catalyst's structural properties, thereby improving its catalytic activity.

1.2.3 Ce-based catalyst

Table 3 gives the commonly seen rare earth-based oxide catalysts for the glycerol carbonylation with CO_2 . Su et al.^[22] investigated the activity of different oxides (ZnO , TiO_2 , ZrO_2 , Al_2O_3 , CeO_2) in this reaction using 2-cyanopyridine as the coupling agent and observed that CeO_2 exhibited the best activity. Subsequently, they evaluated the catalytic performance of CeO_2 with different morphologies (mesoporous, nanotubes, nanorods, nanowires, nanopolyhedra). Under the conditions of using 2-cyanopyridine as the coupling agent, 170 °C, 10 MPa CO_2 , and a reaction time of 12 h, the yield of glycerol carbonate reached 14.2% with CeO_2 nanopolyhedra. Additionally, Liu et al.^[40] prepared the CeO_2 catalysts with various

morphologies *via* precipitation, hydrothermal, and citrate gel methods, and investigated the effect of calcination temperature on the catalyst morphology. The results showed that CeO_2 nanorods synthesized *via* the hydrothermal method and calcined at 400 °C exhibited a relatively high specific surface area, pore volume, and pore size, along with smaller crystallite size and a greater number of surface oxygen vacancies, leading to superior catalytic activity. The redox properties and acid-base characteristics of CeO_2 significantly influence its activity. Under optimal reaction conditions, using 2-cyanopyridine as the dehydrating agent and dimethylformamide as the solvent, the glycerol conversion reached 38%, with a glycerol carbonate yield of 33.3%. Gao et al.^[41] prepared the CeO_2 nanocrystals with different crystal structures, among which the CeO_2 nano-octahedra dominated by the [111] crystal plane demonstrated better catalytic performance than the CeO_2 nanorods [110] and the nanocubes [100]. Simultaneously, computational simulations confirmed that the cyclization step is the rate-determining step, with the CeO_2 [111] surface exhibiting the lowest overall activation energy, which aligns with the superior catalytic performance of CeO_2 nano-octahedra. The catalyst's activity shows a certain linear correlation with the surface base density. This study provides guidance for the future development of CeO_2 -based catalysts. Additionally, mesoporous CeO_2 single-crystal particles prepared *via* ionic liquid regulation also demonstrated favorable catalytic performance for the

glycerol carbonate synthesis. Under relatively low CO₂ pressure (0.5 MPa), a glycerol carbonate yield of 59.1% was achieved. The catalytic activity was positively correlated with the concentration of weak acidic and weak basic sites on the catalyst surface, indicating that weak basic sites (surface hydroxyl groups) and surface defects can act as active centers to promote the activation of polyols and CO₂, synergistically facilitating the formation of cyclic carbonates^[42].

The aforementioned studies indicate that the catalytic activity of CeO₂ is related to its morphologies and crystal structures, which can modulate the specific surface area, crystallite size, pore size, and other properties. Additionally, introducing a second component to prepare materials with special structures can also enhance the catalytic performance. Liu et al. prepared CeO₂-ZrO₂ solid solution catalysts with varying ratios *via* the hydrothermal method. Compared with pure CeO₂, an initial increase followed by a decrease in the specific surface area, pore volume, and surface acid-base quantity was observed with the increase of the Zr content. When the Zr content was 0.02, the catalytic activity reached its peak, with glycerol conversion at 40.9% and glycerol carbonate yield at 36.3%. Fourier transform infrared spectroscopy (FT-IR) results indicated that CO₂ was mainly adsorbed and activated on the catalyst surface in the form of chelating bidentate carbonate. Post-reaction characterization revealed the presence of cerium glycerolate intermediate species on the catalyst surface, based on which a reaction mechanism was proposed (Figure 7). CO₂ and glycerol are adsorbed and activated on the CeO₂ surface, and the activated CO₂ inserts into the

activated glycerol to form a seven-membered ring intermediate species. This intermediate then undergoes intramolecular rearrangement to produce glycerol carbonate, while 2-cyanopyridine reacts with water under the influence of the catalyst to form 2-picolinamide^[43].

Kulal et al.^[44] synthesized CeO₂ nanorods modified with other metals (Ni, Cu, Zn) *via* the hydrothermal method. With the introduction of Ni, Cu and Zn, the crystallite size of CeO₂ decreased, indicating the formation of more defects on the CeO₂ surface. Raman spectroscopy revealed that the incorporation of Zn generated a higher number of oxygen vacancies in CeO₂, which improved the adsorption and activation of CO₂. Furthermore, Zn promoted the transformation of Ce⁴⁺ to Ce³⁺ in CeO₂, partially compensating for lattice contraction through the insertion of Zn with a smaller ionic radius. The chemical adsorption of CO₂ on the catalyst increased with the concentration of surface oxygen vacancies associated with Ce³⁺. The catalytic activity followed the order: Zn/CeO₂ > Ni/CeO₂ > Cu/CeO₂ > CeO₂ nanorods, which aligned with the trend in the CO₂ adsorption capacity. The 10.5% Zn/CeO₂ catalyst exhibited the best performance, achieving a glycerol conversion of 90.4% and a glycerol carbonate yield of 89.5% under optimal reaction conditions.

CeO₂ exhibits significant advantages in the direct catalytic synthesis of glycerol carbonate from glycerol and CO₂ due to its tunable acid-base properties and abundant surface oxygen vacancies. Studies indicate that the catalytically active centers are positively correlated with the concentration of surface oxygen vacancies (Ce³⁺), weak basic sites (such as surface hydroxyl groups), and weak acidic sites.

Table 3 Rare earth-based oxide catalysts for the glycerol carbonylation

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
CeO ₂ -nanopolyhedra	170 °C, 10 MPa-CO ₂ , 12 h	2-cyanopyridine	35.5	14.2	[22]
CeO ₂	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	38	33.3	[40]
CeO ₂ -ZrO ₂	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	40.9	36.3	[43]
ZnO-CeO ₂	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/dimethylformamide	90.4	89.5	[44]
La ₂ O ₃	160 °C, 4.5 MPa-CO ₂ , 18 h	hexanedinitrile	58	9.9	[45]
La ₂ O ₂ CO ₃	160 °C, 4.5 MPa-CO ₂ , 18 h	hexanedinitrile	57.1	10.4	[46]
La ₂ O ₃ /ZIF-8	150 °C, 0.7 MPa-CO ₂ , 15 h	acetonitrile	46.5	35.3	[47]
La ₂ O ₃ /ZIF-8	150 °C, 0.7 MPa-CO ₂ , 15 h	MgCO ₃	35	32.5	
LaCoO ₃	150 °C, 3 MPa-CO ₂ , 12 h	2-cyanopyridine/dimethylformamide	26.3	19.0	[48]

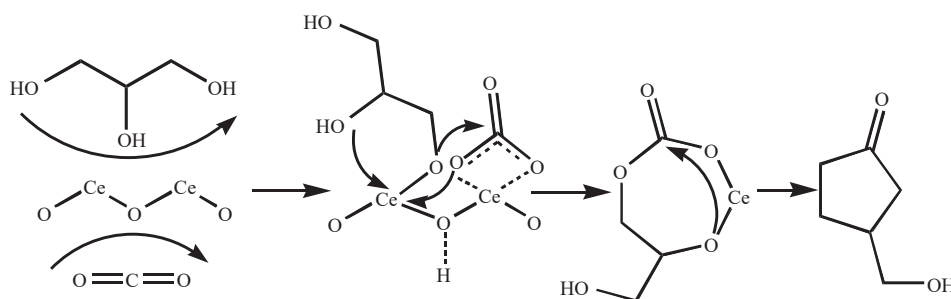


Fig. 7 Possible reaction mechanism for the glycerol carbonylation with CO₂ over CeO₂ based catalysts

These sites can synergistically activate CO₂ (forming chelating bidentate carbonates) and glycerol (forming cerium glycerolate intermediates), thereby reducing the activation energy of the rate-limiting cyclization step. The introduction of metal ions such as Zn and Ni can effectively reduce the crystallite size of CeO₂, induce more oxygen vacancies and Ce³⁺ species, and enhance the chemical adsorption and activation capacity of CO₂. Among these, Zn doping has shown particularly outstanding performance, significantly increasing the yield of glycerol carbonate to nearly 90%. Future research could focus on fine-tuning the concentration of surface oxygen vacancies and the Ce³⁺/Ce⁴⁺ ratio through post-synthesis treatments such as calcination in different atmospheres, plasma treatment, or reduction treatments, aiming to maximize active sites. Building on the notable success of Zn doping, further exploration of other low-cost doping metals (e.g., Co, Mn, Fe) that can effectively modulate the electronic structure of CeO₂ and promote oxygen vacancy generation would be valuable.

1.2.4 La-based catalyst

La₂O₃ has also been applied in the carboxylation of glycerol with CO₂ to synthesize glycerol carbonate. Using hexanedinitrile as the coupling agent, the effects of crude glycerol (containing impurities such as water, methanol, sodium methoxide, and fatty acid methyl esters) and pure glycerol as feedstocks on the catalytic performance were investigated. For the crude glycerol, the presence of methanol helped to enhance the selectivity toward the target product, whereas impurities such as water, sodium methoxide, and fatty acid methyl esters led to a rapid increase in the by-products, negatively impacting the glycerol carboxylation reaction^[45].

Razali et al.^[46] investigated the influence of different coupling agents (acetic anhydride, benzonitrile, acetonitrile, and hexanedinitrile) on the reaction activity using La₂O₃ as the catalyst. Compared with the most commonly used dehydrating agent, acetonitrile, hexanedinitrile increased the yield of glycerol carbonate by fivefold. This effect can be partially attributed to the dinitrile structure of hexanedinitrile. Additionally, hexanedinitrile plays a key role in suppressing the by-product formation and enhancing the mass transfer effect resulting from improved CO₂ solubility. Furthermore, researchers prepared La₂O₂CO₃ via co-precipitation, hydrothermal, and sol-gel methods and found that the catalyst synthesized by co-precipitation exhibited the best activity, achieving a glycerol conversion of 57% and a glycerol carbonate selectivity of 18% when using hexanedinitrile as the coupling agent.

Hu et al.^[47] prepared La nanocluster-modified ZIF-8; the large specific surface area of ZIF-8 facilitates uniform distribution of La on the zeolite surface, while the La³⁺-O²⁻ pairs enhance the acidity and basicity of the catalyst, improving its ability to activate glycerol and CO₂. Using acetonitrile as the coupling agent and 5La/ZIF-8 as the catalyst, the glycerol conversion and glycerol carbonate

yield reached 46.5% and 35.3%, respectively. Additionally, the investigation of the effects of coupling agents such as MgCO₃, H₂SO₄ and CaCO₃ on the reaction indicated that MgCO₃ as a coupling agent significantly enhanced product selectivity. When CH₃CN and MgCO₃ were used as the dehydrating agents, the CO₂/glycerol conversion followed a second-order reaction, with activation energies of 7.83 and 5.42 kJ/mol, respectively. Acetonitrile as a coupling agent requires a higher activation energy and reaction temperature, leading to increased by-product formation and reduced product selectivity. In contrast, MgCO₃ as a coupling agent could improve the product selectivity.

Perovskite-structured LaMO₃ (M = Fe, Co, Ni) catalysts were prepared *via* the sol-gel method. The transition metals in these catalysts exhibit multiple valence states, leading to unique surface properties such as oxygen defects. Among them, LaNiO₃ showed the highest concentration of oxygen vacancies, while La₂O₃ had the fewest. Additionally, the CO₂-TPD results indicated that the number of weak and medium basic sites for different catalysts followed the order of LaCoO₃ > LaNiO₃ > LaFeO₃ > La₂O₃. LaCoO₃ demonstrated the best catalytic performance, primarily due to its higher number of weak and medium basic sites. However, strong basic sites tend to promote side reactions, reducing the selectivity of glycerol carbonate^[48].

The La-based catalysts demonstrate potential in the synthesis of glycerol carbonate from glycerol and CO₂, with their performance influenced by both the catalyst structure (basicity, oxygen vacancies) and the type of coupling agent (hexanedinitrile, acetonitrile, MgCO₃, 2-cyanopyridine). By adjusting the catalyst structure (e.g., perovskite-type LaMO₃), enhancing La dispersion (e.g., La/ZIF-8), and improving surface acidity-basicity, the catalytic activity can be significantly enhanced. Moreover, employing different coupling agents can optimize the product selectivity. For instance, using MgCO₃ as a coupling agent achieves a glycerol carbonate selectivity up to 93%, markedly outperforming acetonitrile, hexanedinitrile, and 2-cyanopyridine. Future research should focus on the precise regulation of the surface properties of La-based catalysts, such as through the fabrication of composite metal oxides with tailored morphologies, to further improve the catalytic activity.

1.2.5 Mg-based catalyst

Table 4 gives the commonly seen Mg-based catalysts for the glycerol carbonate synthesis from glycerol and CO₂. Among MgO, CaO and Al₂O₃ prepared using the precipitation method, MgO exhibited a relatively large specific surface area and pore volume, facilitating the exposure of more active sites. Additionally, MgO displayed the highest total basicity, primarily composed of strong and weak basic sites. CaO showed comparable total basicity to MgO, but its basic sites were mainly of medium strength. γ-Al₂O₃ had the lowest total basicity, and similar to MgO, its basic sites were predominantly strong and weak.

Table 4 Mg-based catalysts for the glycerol carbonate synthesis from glycerol and CO₂

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
MgO	150 °C, 8.0 MPa-CO ₂ , 24 h	2-cyanopyridine/dimethylformamide	22.7	12.76	[49]
MgCaO	180 °C, 7 MPa-CO ₂ , 24 h	2-cyanopyridine/dimethylformamide	25.7	16	[50]
MgInCe-MMO	170 °C, 4 MPa-CO ₂ , 12 h	2-cyanopyridine/dimethylformamide	14.6	14.5	[51]
MgZnCe	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/ <i>N</i> -methylpyrrolidone	90	58	[52]
MgPSCN	250 °C, 1 MPa-CO ₂ , 4 h	acetonitrile	68.72	44.9	[53]

The catalytic activity of these three oxides followed the order of MgO > CaO > Al₂O₃, which correlated with the number of basic sites on the catalyst surface. It was also observed that both the quantity of basic sites and the BET surface area of the catalyst significantly impact the catalytic performance for this reaction^[49].

To further modulate the surface acidity-basicity and specific surface area of the catalysts, bimetallic composite oxide catalysts including MgCa, MgAl and CaAl were prepared *via* the co-precipitation method. The MgAl oxide mainly existed in the cubic phase of MgAl₂O₄^[50]. In the CaAl oxide, in addition to CaO, phases such as Ca₁₂Al₁₄O₃₃ and CaAl₂O₄ were also observed. The MgCa oxide primarily consisted of MgO and CaO phases. The MgCa catalyst exhibited a relatively large specific surface area, allowing for the exposure of more active sites. The MgAl and CaAl catalysts had a higher number of surface basic sites, predominantly strong basic sites. In contrast, although the total number of basic sites on the MgCa surface was relatively lower, they consisted mainly of weak and medium-strength basic sites, with little strong basic sites. Under identical compositional conditions, the MgCa catalyst demonstrated the best performance. Furthermore, the optimization results of MgCa composition indicated that as the Mg content increased, the specific surface area gradually increased, with Mg_{0.75}Ca_{0.25}O exhibiting a relatively large specific surface area, pore size and pore volume. The basicity of the catalyst increased with higher Mg content, and the strength of the basic sites was also enhanced. The number of strong basic sites in Mg_{0.75}Ca_{0.25}O rose rapidly, reaching 1904.5 μmol/g. The higher the Mg content in the MgCa catalyst, the higher the reaction activity. When the Mg/Ca ratio increased from 1:3 to 1, the glycerol conversion increased from 14.8% to 18.2%. The catalytic activity was positively correlated with the specific surface area, surface basicity, and quantity of basic sites. By optimizing the reaction conditions at 180 °C and a CO₂ pressure of 7 MPa, the glycerol conversion reached 25.7%, and the glycerol carbonate yield was 16%^[50].

To increase the number of oxygen vacancies in the material, researchers introduced other valence-variable metals to prepare trimetallic composite oxide catalysts. Chen et al.^[51] synthesized highly dispersed MgInCe composite metal oxides using hydrotalcite as the precursor. After calcination at 500 °C, well-crystallized MgIn₂O₄ was formed, while lower calcination temperatures resulted in a poorer crystal structure of MgIn₂O₄. The incorporation of In led to the formation of more In–O vacancies on the material

surface, facilitating the adsorption and activation of CO₂. The introduction of Ce created Mg–O–Ce acid sites, enhancing the activation capability for glycerol. As a result, under the synergistic effect of acid-base sites, the catalyst exhibited excellent activity, with glycerol carbonate selectivity reaching up to 99%. The activation process of CO₂ and glycerol on the catalyst was investigated using FT-IR, and a possible reaction mechanism was proposed (Figure 8): adjacent Mg–O–Ce sites and In–O vacancy sites provide synergistic effects. (1) Mg–O–Ce sites activate glycerol in a dual-activation mode, (2) In–O vacancy sites simultaneously adsorb CO₂ in a bidentate activation mode, and (3) high dispersion at the atomic level promotes the insertion of activated CO₂ into the five-membered ring glycerol intermediate.

Furthermore, Pattanaik et al.^[52] prepared the Mg–Zn–Ce composite metal oxide catalysts using the co-precipitation method. The introduction of an appropriate amount of Mg into Zn/Ce oxides promoted the formation of a solid-solution structure, which facilitated the generation of more oxygen vacancies on the surface and also improved the specific surface area. The surface of the Mg–Zn–Ce catalyst exhibited both Brønsted and Lewis acid structures. Compared to other materials, the 10Mg/10Zn/CeO₂ catalyst possessed the highest number of acid and base sites. The ternary oxides, 10Mg/10Zn/CeO₂, in particular, demonstrated higher glycerol conversion and glycerol carbonate yield. A high concentration of surface oxygen vacancies, sufficient acid-base strength, and a larger surface area are effective means to enhance catalytic performance. Under optimal reaction conditions, the glycerol conversion reached 90%, with a glycerol carbonate yield of 58%. The catalyst was easily separable and reusable, showing no significant loss in activity after five consecutive cycles.

Charif et al.^[53] prepared phosphorus (P), sulfur (S), magnesium (Mg), and lithium (Li) doped graphitic carbon nitride (g-C₃N₄). Doping with these elements reduced the crystallinity of C₃N₄, decreased crystallite size, widened pore channels, and increased pore volume. Compared to pure C₃N₄, the incorporation of phosphorus and sulfur altered the electronic properties and enhanced Lewis basicity. Relative to LiPSCN, the MgPSCN catalyst exhibited better thermal stability and demonstrated superior catalytic performance, achieving a maximum glycerol conversion of 70.05% and a maximum glycerol carbonate (GC) yield of 45.85%. The gradual decline in activity after catalyst reuse was primarily attributed to the detachment of active particles from the carbon nitride surface.

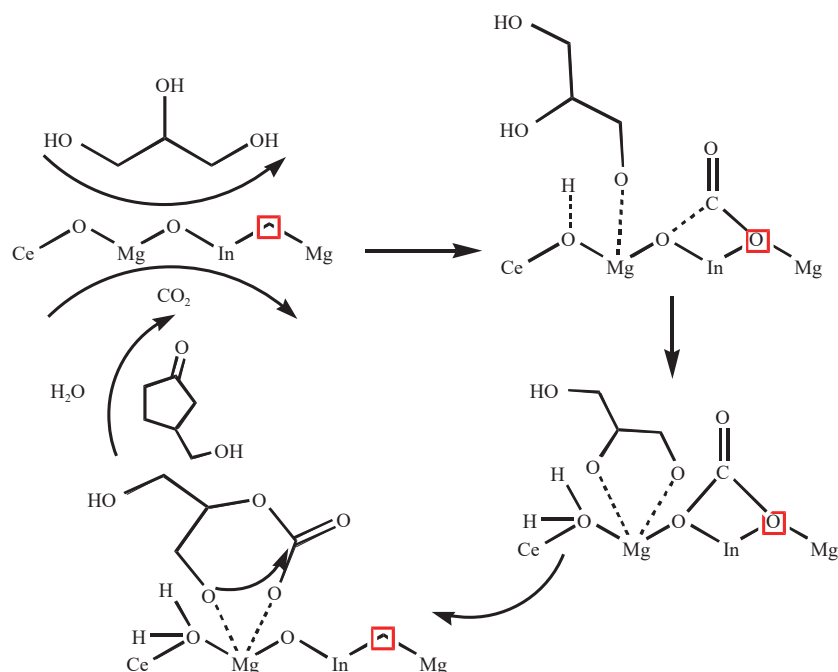


Fig. 8 Synergistic catalytic mechanism of MgInCe mixed metal oxides for the glycerol carbonate synthesis from glycerol and CO₂

Compared to MgO, composite metal oxides exhibited enhanced catalytic activity. Among binary composite oxides such as Mg-Ca and Mg-Al, the Mg-Ca system, dominated by weak to medium-strength basic sites, demonstrated superior performance to Mg-Al and Ca-Al systems containing strong basic sites. This indicates that the distribution of base strength is more critical than the total base quantity alone. A larger specific surface area, appropriate pore size, and pore volume are essential for exposing sufficient active sites and promoting reactant diffusion. Multicomponent composite oxides (e.g., Mg-Zn-Ce) possess characteristics such as a high concentration of oxygen vacancies, bifunctional acid-base sites, and a large specific surface area, achieving high activity (glycerol conversion up to 90%) and good stability. Heteroatom-doped g-C₃N₄ (e.g., with P, S, Mg, Li) also displayed favorable catalytic activity by modulating the electronic structure and basicity, though its stability (e.g., active component detachment) remains a key challenge to address.

Future research could focus on designing acid-base sites with atomic-scale proximity and spatially matched structures, such as metal-oxygen pairs (acidic sites) coupled with basic sites/oxygen vacancies, by utilizing well-defined precursors like hydrotalcite, spinel, or perovskite to fabricate highly dispersed and structurally stable bifunctional or multifunctional active centers. Building on

the proven effectiveness of systems like Mg-Ca and Mg-Zn-Ce, further exploration of introducing other metal elements (e.g., Fe, Co, Ni, Mn) to modulate the surface oxygen vacancies and acid-base properties could lead to further improvements in the catalytic activity.

1.2.6 Noble metal catalyst

Table 5 gives the commonly seen noble metal catalysts for the glycerol carbonate synthesis from glycerol and CO₂. Ozorio et al. prepared AgY, ZnY and SnY catalysts by impregnating metal nitrates on the surface of NaY zeolite. Among them, AgY exhibited the highest glycerol conversion, primarily attributed to the high dispersion of Ag on the zeolite surface^[54].

Lukato et al.^[55] loaded Au onto a cerium-based metal-organic framework (MOF) using different methods. When MgCO₃, acetonitrile, and hexanedinitrile were used as the dehydrating agents, MgCO₃ showed the best performance. After reduction with hydrogen, the 4% Au@MOF catalyst achieved a glycerol conversion of 52% and a glycerol carbonate yield of 44% under a CO₂ pressure of 1.5 MPa. The high selectivity of this catalyst is likely related to the small and uniformly distributed Au nanoparticles within the MOF cavities.

Table 5 Noble metal catalysts for the glycerol carbonate synthesis from glycerol and CO₂

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
Ag-Y	180 °C, 7.0 MPa-CO ₂ , 3 h	—	—	5.6	[54]
4% Au@Ce-MOF	150 °C, 1.5 MPa-CO ₂ , 13 h	MgCO ₃ /MeOH-dimethylformamide	52	44	[55]
Au/ZnWO ₄ -ZnO	150 °C, 8.0 MPa-CO ₂ , 5 h, 225 W visible light irradiation	—/dimethylformamide	10.6	10.6	[56]
Au/Co ₃ O ₄ -ZnO	150 °C, 5 MPa-CO ₂ , 6 h, 225 W visible light irradiation	—/dimethylformamide	6.5	6.5	[57]

Au nanoparticles exhibit strong surface plasmon resonance (SPR) in the visible region, enabling efficient capture of visible light to generate high-energy hot electrons and holes, thereby enhancing catalytic activity through photothermal synergy. Liu et al.^[56] prepared a series of Au/ZnWO₄-ZnO catalysts *via* the impregnation method. The results showed that a certain interaction was formed between Au and Zn. As the Au content increased, the ZnO particle size gradually increased, while the specific surface area and total surface basicity of the catalyst decreased. Furthermore, the introduction of Au enhanced the visible-light absorption intensity of the catalyst. Excitation by visible light promoted the generation of photogenerated electron-hole pairs, which facilitated the adsorption and activation of CO₂ and glycerol. This process suppressed the desorption of CO₂ under high temperature and improved the selectivity toward the target product. Building on this, they further prepared a series of Au/Co₃O₄-ZnO catalysts and found that the heterojunction structure of Au/Co₃O₄-ZnO facilitated the visible-light absorption and promoted the separation of electron-hole pairs. Additionally, the loading of Au altered the electron density of Co and Zn, enhancing the reducibility of Co and increasing the number of oxygen vacancies on the Co₃O₄-ZnO surface. The localized surface plasmon resonance (LSPR) effect of Au nanoparticles strengthened the visible-light absorption capacity of Au/Co₃O₄-ZnO and improved the separation of photogenerated electron-hole pairs, thereby enhancing the photothermal catalytic performance^[57]. This approach, leveraging photothermal synergy, offers a new direction for the development of highly efficient catalysts.

Currently, research on the noble metal catalysts mainly focuses on Au-based systems. By supporting Au on metal oxides or MOF materials, the dispersion of Au can be enhanced. Additionally, the electronic interaction between Au and the carrier modulates the reducibility of the support and the concentration of surface oxygen vacancies. The localized surface plasmon resonance (LSPR) effect of Au enhances visible light absorption and promotes the separation of photogenerated carriers, while photothermal synergy improves the reaction efficiency. The introduction of coupling agents significantly increases glycerol conversion and glycerol carbonate yield. However, due to the high cost of noble metals, future efforts should prioritize rational design strategies to improve the dispersion of noble metals, thereby increasing atomic utilization efficiency and reducing loading levels.

1.2.7 Modified zeolite catalyst

Table 6 gives the commonly seen modified zeolite catalysts for the glycerol carbonate synthesis from glycerol and CO₂. The Co-ZIF-67 material prepared by Hu et al.^[58] exhibits high crystallinity, a large specific surface area (1250 m²/g), good thermal stability, facile ligand-to-metal electron transfer, and abundant Lewis basic sites, which contribute to its high catalytic activity in the glycerol carbonylation with CO₂. Using acetonitrile as a coupling agent under 0.3 MPa CO₂, the selectivity to glycerol carbonate reached 92%, with a carbonate yield of 29%. The reaction followed a third-order kinetics and proceeded rather slowly; a longer reaction time favored the progress of this reaction.

Gao et al.^[59] prepared a series of Co, Zn, Cu, Ni, Zr, Ce and Fe-modified ETS-10 catalysts. The introduction of metals led to a slight decrease in the specific surface area of the catalysts, while the number of basic sites on the catalyst surface increased, and the alkali strength decreased. Among them, the Co-modified zeolite displayed little structural damage to the zeolite support. Moreover, the moderate Lewis basic sites of ETS-10 and the synergistic effect of Co played a positive role in activating CO₂ and glycerol. In addition, Co/ETS-10 exhibited good structural integrity and suitable Lewis basic and acidic strengths. Under 170 °C, an initial pressure of 4.0 MPa, 5 mL of CH₃CN and a reaction time of 6 h, the Co/ETS-10 catalyst showed the highest activity, with a glycerol conversion of 35.0% and a carbonate yield of 12.7%.

Hu et al.^[60] prepared Ce-, Cu-, and Mg-modified ZIF-8 catalysts. The introduction of Ce and Cu resulted in isomorphic substitution of Zn in ZIF-8, maintaining the structural integrity of ZIF-8. In contrast, the introduction of Mg disrupted the ZIF-8 structure, leading to the formation of rod-like structures accompanied by irregular and small particles, which exhibited characteristics of a ZIF-8 and metal oxide composite material. The surface alkalinity of all metal-doped catalysts increased, with Mg-modified ZIF-8 showing the most significant increase. The catalytic activity of all metal-modified ZIF-8 catalysts was improved, with Mg-ZIF-8 demonstrating the best reaction performance. The effects of coupling agents such as acetonitrile, CaCO₃, MgCO₃, Na₂SiO₃, CaF₂, CaCl₂ and NaHCO₃ were also investigated, which revealed that using acetonitrile as the coupling agent gave a relatively high glycerol conversion; however, the selectivity to glycerol carbonate was low due to the formation of by-products. In contrast, when NaHCO₃ was used as the coupling agent, the product selectivity reached 91%.

Table 6 Modified zeolite catalysts for the glycerol carbonate synthesis from glycerol and CO₂

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
Co-ZIF-67	210 °C, 0.3 MPa-CO ₂ , 12 h	acetonitrile	32	29	[58]
Co-ETS-10	170 °C, 4.0 MPa-CO ₂ , 6 h	acetonitrile	35	12.7	[59]
Mg-ZIF-8	175 °C, 0.3 MPa-CO ₂ , 6 h	NaHCO ₃	38.7	35.2	[60]

The introduction of other metal oxides can significantly modulate the zeolite surface acidity and alkalinity, offering considerable advantages for the design and optimization of the catalysts for glycerol carbonylation. Currently, the research on zeolite modification remains limited. Although Co-modified ZIF-67 and ETS-10 displayed comparable glycerol conversion, they were rather different in the selectivity to glycerol carbonate. Future studies could focus on these two catalysts to investigate the influence of the physicochemical properties of zeolites on the side reactions, aiming to enhance the selectivity for the target product. Experimental results indicate that the coupling agents have a significant impact on the product selectivity. Although acetonitrile facilitates the primary reaction, it may also promote the side reactions. In contrast, inorganic coupling agents such as NaHCO_3 can efficiently remove water molecules, shift the reaction equilibrium toward the product side, and achieve high selectivity ($> 90\%$) to glycerol carbonate. Future work could explore modifications using different basic zeolites (e.g., SBA-15, ZSM-5, X- and Y-type zeolites) and the effects of various coupling agents (e.g., 2-cyanopyridine, adiponitrile) on the glycerol carbonylation reaction.

1.2.8 Other heterogeneous catalyst

Besides abovementioned catalysts, some other catalysts are also used in the glycerol carbonate synthesis from glycerol and CO_2 , as given in Table 7. The Ti-Al-Mg, Ti-Cr-Mg and Ti-Fe-Mg series catalysts were prepared *via* co-precipitation^[61]. The trivalent metal ions Al, Cr and Fe can modify the acid-base properties and electronic environment around Mg on the catalyst surface, thereby modulating the catalytic performance. Compared to Ti-Cr-Mg and Ti-Fe-Mg, a ternary oxide $\text{MgAl}_2\text{Ti}_3\text{O}_{10}$ was formed in Ti-Al-Mg, where Mg^{2+} ions had different neighboring cations (Al^{3+} and Ti^{4+}), creating a more electron-rich environment and donating electrons to the Mg^{2+} ions through an inductive effect; this could weaken the basic characteristic of Mg^{2+} . Ti-Al-Mg exhibited the highest low-temperature CO_2 adsorption capacity and the lowest CO_2 binding energy on its surface, thus facilitating CO_2 adsorption and activation. The activated CO_2 was also easily desorbed and could subsequently participate in the reaction. The Ti-Cr-Mg and Ti-Fe-Mg catalysts exhibited limited porosity and a dense structure, which restricted the diffusion of reactants; in contrast, the surface of the Ti-Al-Mg catalyst was porous, rough, and composed of irregularly shaped particles,

featuring a layered yet dense structure with a relatively large specific surface area. The extended pore network and interparticle voids facilitated effective molecular diffusion, while the roughness and porosity provided a substantial number of exposed active sites, enabling efficient adsorption and activation of reactants. Consequently, the Ti-Al-Mg catalyst demonstrated the highest catalytic activity, achieving a glycerol carbonate yield of 36.1%^[61].

Furthermore, mesoporous CeLaCo perovskite-type composite metal oxides have also been employed in the glycerol carbonylation reaction. After calcination at 700 °C, this material develops a higher number of strong basic and acidic sites on its surface. By using ZSM-5 zeolite membranes with different Si/Al ratios as the physical water-removing membrane, the catalytic reaction efficiency is significantly enhanced. As the Si/Al ratio of the ZSM-5 membrane decreases, the increased concentration of Na^+ -gated channels facilitates preferential water separation, leading to continuous improvement in the glycerol conversion and glycerol carbonate yield. Additionally, the ZSM-5 membrane demonstrates good reusability in the coupled reaction-separation process^[62]. This research provides novel insights for the development of physical dehydration processes.

Collett et al.^[63] utilized rice husks (RH), oilseed rape straw (OSR), softwood pellets (SWP), and wheat straw pellets (WSP) to prepare biochar materials for the catalytic synthesis of glycerol carbonate. The SWP-derived biochar did not contain metallic elements, whereas the carbon materials prepared from other feedstocks contained elements such as Si, K, Ca and Mg. Furthermore, significant differences exist in the specific surface area and micropore volume of the materials. Activity test results show that SWP biochar and activated carbon had no activity for this reaction, while other biochar materials demonstrated certain catalytic activity. Moreover, biochar materials with higher ash content showed better catalytic performance. The K content played a crucial role in the catalytic activity, with RH-550 demonstrating the most favorable catalytic performance.

Fao et al.^[64] prepared P- and S-doped graphitic carbon nitride (PSCN) catalysts. The doping of P and S improved the Lewis acid-base sites on the catalyst surface, thereby promoting the glycerol carbonylation reaction. The co-doping of P and S enhanced CO_2 adsorption and facilitated the separation of e^- - h^+ pairs, resulting in a higher reaction rate over PSCN compared to that over unmodified CN.

Table 7 Other catalysts for the glycerol carbonate synthesis from glycerol and CO_2

Catalyst	Reaction conditions	Coupling agent/Reaction solvent	Glycerol conv./%	GC yield/%	Reference
Ti-Al-Mg	175 °C; 1 MPa- CO_2 , 4 h	acetonitrile	58.3	36.1	[61]
CeLaCo-MMO	150 °C, 4 MPa- CO_2 , 12 h	ZSM-5 zeolite membrane	40.1	25.18	[62]
Bio-based carbon material	160 °C, 3.0 MPa- CO_2 , 22 h	acetonitrile	—	—	[63]
P-S-g- C_3N_4	210 °C, 0.3 MPa- CO_2 , 6 h	acetonitrile	85	—	[64]

Furthermore, density functional theory (DFT) calculations indicated that the effective charge transfer induced by P and S doping could reduce the activation barrier for the carboxylation, enhancing the catalytic activity. This provides a promising catalyst for the CO₂/glycerol conversion.

Among the aforementioned catalysts, biochar prepared from biomass exhibits certain catalytic activity for this reaction, primarily attributed to the alkali metal ions, especially potassium, present in the biochar. This indicates that such catalysts are essentially metal-based in nature. Meanwhile, P- and S-doped C₃N₄ demonstrates a relatively high glycerol conversion under lower reaction pressure, offering new insights for the development of novel catalysts. Additionally, the use of ZSM-5 zeolite membranes to enhance water separation and improve reaction performance provides a novel pathway for reaction-separation coupling. Future research could focus on exploring the photothermal synergistic catalytic properties of C₃N₄ non-metallic catalysts, while optimizing coupling agents and reaction solvents to further enhance the catalytic activity. The ZSM-5 zeolite membrane reaction process is green and efficient, making it potentially applicable to other catalytic systems and thereby advancing the development of this synthesis route.

1.2.9 Comparative discussion on different types of catalysts

Table 8 summarizes the best-performing catalysts among Zn-, Cu-, Ce-, La- and Au-modified zeolites and non-metallic materials. Among these, ZnO-CeO₂ exhibits the highest activity, achieving a selectivity of 99% to glycerol carbonate and a yield of 89.5% under the conditions using 2-cyanopyridine as the coupling agent and *N,N*-dimethylformamide as the solvent. This performance is

comparable to that of the homogeneous Zn(OTf)₂ catalyst. Under nearly identical conditions, CuO and MgZnCe catalysts show similar glycerol conversions, but they differ significantly in the product selectivity, indicating a substantial influence of the catalyst on product distribution. Zeolites, with their large specific surface areas, can significantly enhance the dispersion of active components, thereby improving catalytic activity. La₂O₃/ZIF-8 and Mg-ZIF-8 also demonstrate good activity for this reaction; however, compared to the Zn-based catalysts, they display much lower glycerol conversion and product yield, which may be attributed to the differences in the intrinsic properties of their active sites. Although Au, as a noble metal catalyst, achieves high dispersion when supported on MOF materials, it does not show a distinct activity advantage. The results above indicate that Zn-based catalysts exhibit a clear activity advantage for this reaction and currently hold the greatest potential for industrial application.

Furthermore, when La₂O₃/ZIF-8 was used as the catalyst and acetonitrile as the coupling agent, the highest product selectivity observed was 76%. In contrast, other coupling agents achieved a selectivity above 90%, with 2-cyanopyridine notably reaching 99%. Thus, acetonitrile is not an ideal choice as the coupling agent, which aligns with theoretical calculation results^[20]. Additionally, the use of polar solvents such as *N,N*-dimethylformamide or *N*-methylpyrrolidone resulted in significantly higher glycerol conversions, indicating that polar solvents facilitate the activation of glycerol or CO₂ and promote the progress of the carbonylation reaction.

Although ZnO-CeO₂ exhibited high catalytic activity under the conditions using 2-cyanopyridine as the coupling agent and dimethylformamide as the solvent, the reaction system is complex, involving lengthy subsequent product separation processes, and the high cost of 2-cyanopyridine poses a challenge.

Table 8 Comparison of different catalysts in their activity for the glycerol carbonate synthesis from glycerol and CO₂

Catalyst	Reaction conditions	Coupling agent/ Reaction solvent	Glycerol conv./%	GS sel./%	GC yield/%	Reference
Zn(OTf) ₂	180 °C, 5 MPa-CO ₂ , 24 h	CaC ₂ /1-methyl-2-pyrrolidinone	—	—	92	[23]
ZnAlCe	170 °C, 4.5 MPa-CO ₂ , 12 h	acetonitrile	56.7	51	28.9	[31]
CuO	120 °C, 3 MPa-CO ₂ , 5 h	2-cyanopyridine/ <i>N,N</i> -dimethylformamide	89	70	61.7	[34]
ZnO-CeO ₂	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/ <i>N,N</i> -dimethylformamide	90.4	99	89.5	[44]
MgZnCe	150 °C, 4 MPa-CO ₂ , 5 h	2-cyanopyridine/ <i>N</i> -methylpyrrolidone	90	65	58	[52]
La ₂ O ₃ /ZIF-8	150 °C, 0.7 MPa-CO ₂ , 15 h	acetonitrile	46.5	76	35.3	[47]
		MgCO ₃	35	93	32.5	
Mg-ZIF-8	175 °C, 0.3 MPa-CO ₂ , 6 h	NaHCO ₃	38.7	91	35.2	[60]
4%Au@Ce-MOF	150 °C, 1.5 MPa-CO ₂ , 13 h	MgCO ₃ /MeOH- <i>N,N</i> -dimethylformamide	52	85	44	[55]
P-S-g-C ₃ N ₄	210 °C, 0.3 MPa-CO ₂ , 6 h	acetonitrile	85	—	—	[64]

For the catalyst optimization, future efforts could focus on modulating the preparation parameters and synthesis methods of ZnO-CeO₂ to achieve unique morphologies such as layered hydroxalite, perovskite, or fluorite structures. Alternatively, mesoporous/porous composite oxides could be synthesized *via* templating methods or by supporting the active components on zeolite surfaces to increase specific surface area and expose more active sites. Additionally, introducing other components (e.g., Fe, Mn) or employing post-treatment techniques (e.g., calcination under different atmospheres, plasma treatment, reduction) could fine-tune the surface oxygen vacancy concentration and Ce³⁺/Ce⁴⁺ ratio, maximizing active site availability and further enhancing catalytic performance. The research on other catalyst types, such as rare earth oxides, zeolites, noble metals, and non-metallic catalysts, remains relatively limited. Systematic studies on their physicochemical properties and reaction mechanisms are needed to build a robust theoretical foundation for the catalyst design. An integrated experimental and computational approach could be adopted to rationally screen coupling agents such as CaC₂, 2-cyanopyridine, MgCO₃, and NaHCO₃. Moreover, novel zeolite membrane reactors could be designed to develop physical separation methods for efficient removal of byproduct water, promoting a greener and more sustainable process.

2 Conclusions and outlook

This article summarizes the research progress over the past two decades on the homogeneous and heterogeneous catalysts for the direct carbonylation of glycerol with CO₂ to synthesize glycerol carbonate. Heterogeneous catalysts are classified in detail based on the differences in the active sites. For each category, the modulation of composition, structural optimization, and physical property parameters are systematically reviewed. Additionally, various coupling agents are compared and analyzed.

(1) Homogeneous Catalysts: Homogeneous catalysts mainly consist of metal-organic complexes and organic bases, which require the synergistic use of coupling agents to achieve favorable catalytic performance. In the reaction process, the use of polar solvents (e.g., *N*-methyl-2-pyrrolidone) that promote the glycerol activation or solvents (e.g., bmimPF₆) that enhance the CO₂ adsorption and activation can significantly improve the reaction activity. Among these, DBU and Zn(OTf)₂ demonstrate notable effectiveness, with glycerol carbonate yields reaching 86% and 92%, respectively. Their superior activity is partially attributed to the favorable contact between the catalysts and reactants. Future efforts could focus on optimizing the structure of ligands and the composition of transition metal complexes to enhance their activity, as well as investigating the effects of other polar solvents (e.g., dimethylformamide, ethylenediamine, *n*-butylamine, etc.) on the reaction performance. Furthermore, using homogeneous catalysts as

models to deeply understand the intrinsic influence of coupling agents and solvents on the reaction, and combining theoretical calculations with experimental characterization to explore reaction mechanisms, can provide valuable insights for the development of efficient heterogeneous catalysts and reaction systems.

(2) Heterogeneous Catalysts: These primarily include Zn-, Cu-, Ce-, La-, Mg-, noble metal (Au and Ag) oxides, zeolite-modified catalysts, and non-metallic catalysts. Among metallic catalysts, metal oxides are the most common. Active components such as Zn, Cu, Ce, La and Mg have been optimized for the reaction performance through various strategies, including tailoring morphologies, forming bimetallic or trimetallic oxides, and tuning properties such as specific surface area, pore size distribution, oxygen vacancy concentration, and surface acidity/basicity. These metal oxides generally follow a similar reaction mechanism: metal sites activate glycerol, while oxygen vacancies serve as basic sites to adsorb and activate CO₂. The activated CO₂ then inserts into the activated glycerol, forming a seven-membered cyclic intermediate, which subsequently undergoes intramolecular rearrangement to yield the target product, glycerol carbonate. Among these, ZnO-CeO₂ exhibits exceptional catalytic performance. Under optimal conditions, with 2-cyanopyridine as the coupling agent and dimethylformamide as the reaction solvent, glycerol conversion and glycerol carbonate yield reach 90% and 89%, respectively. This represents the highest reported performance for the heterogeneous catalysts to date, approaching the activity of the homogeneous catalyst Zn(OTf)₂. The use of an organic base (dimethylformamide) as the solvent enhances CO₂ dissolution and activation, thereby improving the reaction efficiency. Additionally, ZSM-5 zeolite membranes can effectively separate water generated during the reaction, promoting the reaction progress. This offers a novel reaction-separation coupling model for this reaction and other similar processes.

Currently employed coupling agents, such as 2-cyanopyridine, significantly shift the thermodynamic equilibrium but face challenges including high cost and the need for post-treatment of their hydrated products to enable recycling, which hinders their industrial-scale application. Therefore, there is a need to develop more efficient and atom-economical tandem reaction pathways in the future. For the design of heterogeneous catalysts, tailored modulation strategies should be implemented based on the active components to achieve desirable properties such as high specific surface area, appropriate pore size distribution, abundant surface oxygen vacancies, and optimized surface acidity/basicity as well as acid-base site density, thereby enhancing the catalytic performance. Nanostructured bifunctional materials, typically composed of highly dispersed and strongly basic metal oxides supported on carriers with large specific surface areas, can provide more active sites to boost the catalytic activity. Furthermore, novel reactor designs, such as membrane reactors, can be

employed to drive the reaction forward by removing water, thereby increasing the reaction rate. Integrating experimental characterization with theoretical calculations to elucidate the adsorption and activation pathways of CO₂ and glycerol in polar solvents will also contribute to improving reactant adsorption and activation, synergistically enhancing the reaction efficiency. With continued in-depth research, it is anticipated that more novel catalysts, coupling agents, and reaction solvents will be developed, ultimately facilitating the industrialization of this reaction process.

Declaration of Competing Interest

The authors declare no conflict of interest.

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CO₂与甘油直接羰基化合成甘油碳酸酯催化剂研究进展

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摘要: 二氧化碳(CO₂)羰基化制甘油碳酸酯是实现CO₂资源化利用的有效途径, 既能缓解碳排放压力, 又能合成高附加值化学品。然而, 该反应过程受热力学平衡限制, 甘油转化率和碳酸酯收率较低, 因此, 需引入耦合剂并开发高效催化剂。本工作系统综述了近年来CO₂与甘油直接羰基化制甘油碳酸酯的均相催化剂(无机碱和有机碱)和非均相催化剂(Zn、Cu、Ce、La、Mg、贵金属、分子筛改性以及非金属材料等)的研究进展, 分析了金属氧化物改性、载体优化、前驱体选择、酸碱位构筑等策略对提升催化剂性能的作用机制, 总结了不同耦合剂(乙腈、己二腈、2-氰基吡啶、MgCO₃、CaC₂、NaHCO₃等)的作用效果, 并提出了催化剂的设计思路。未来提升甘油与CO₂羰基化合成甘油碳酸酯效率可采取的措施包括: 设计有机金属络合物或具有高分散性、特殊形貌结构的复合金属氧化物等策略, 调变催化剂的比表面积、孔径和表面酸碱性; 优化耦合剂或设计新型膜反应器促进反应进行; 引入极性反应溶剂等措施提高原料的吸附活化能力, 提升反应活性。

关键词: CO₂; 甘油; 羰基化; 甘油碳酸酯; 催化剂

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