

## Review Article

# Progress of Catalytic Valorization of Bio-Glycerol with Urea into Glycerol Carbonate as a Monomer for Polymeric Materials

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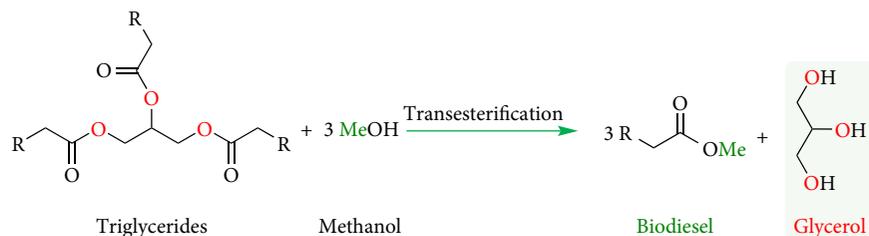
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Versatile polymers with highly adjustable characteristics and a broad range of applications are possibly developed owing to the contemporary industrial polymerization techniques. However, industrial production of large amounts of chemicals and polymers heavily depends on petroleum resources which are dwindling and unsustainable. Of particular interest is to utilize sustainable and green resources for the manufacture of polymeric materials. The efficient transformation of bio-glycerol to the relevant functional derivatives are being widely investigated owing to the increasing demand for enhancing the value of glycerol manufactured by biodiesel and oleochemical industries. With respect to glycerol-based polymer chemistry and technology, considering the economy and environmental benefits, using effective catalysts for the selective transformation of bio-glycerol and urea into glycerol carbonate (GC) as a polymer monomer is of great significance. In this review, recent studies on GC synthesis involving the catalysts such as zinc, magnesium, tungsten, ionic liquid-based catalysts, reaction conditions, and possible pathways are primarily described. Some critical issues and challenges with respect to the rational development of heterogeneous catalytic materials like well-balanced acid-base sites are also illustrated.

## 1. Introduction

Modern life depends on polymers, from materials applied in the manufacture of clothing, houses, cars, and airplanes to those demonstrating complex adhibitions in medicine, diagnostics, and electronics [1–4]. A vast majority of polymers have been contributing greatly to our better daily life of enhanced quality and cleaner living environments, for instance, as materials capable of purifying water or as polymers bearing the better fuel economy in aerospace utilizations. Nonetheless, most of these polymers are supplied by the traditional petrochemicals. It is reported that merely 6% of the oils furnished globally are used to produce polymers, but the raw resources and their end-of-life options will arouse the important environmental issues [5]. Since there is no panacea for these sophisticated environmental concerns, one

alternative is to exploit more “sustainable” polymers. Research has been focusing basically on developing the renewable feedstocks to substitute fossil raw sources and on opening-up the end-of-life options that can provide materials that are feasible in recycling or biodegradation [6, 7]. As polymers are derived from sustainable biomass resources, they are generally deemed to be bioderived. It should be recognized that with respect to the concept of biodegradation, some petrochemical-derived polymers are also biodegradable, while some bioderived polymers will not biodegrade [8]. Generally, two procedures are used to prepare sustainable polymers: decreasing the environmental influence of traditional manufacture, such as by employing biomass materials for the manufacture of known monomers or polymers like polyethylene terephthalate and polyethylene; and preparing the novel, and “sustainable” structures like polylactide from renewable resources that are applied

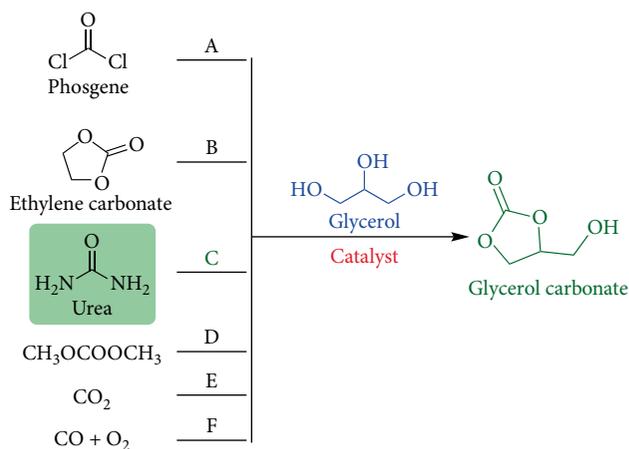


SCHEME 1: Catalytic transesterification of triglycerides to biodiesel and glycerol.

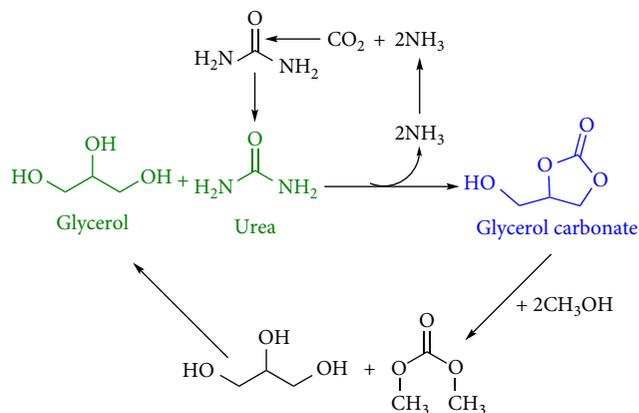
increasingly for preparing polymers [9, 10]. Specifically, the vital monomers including carbon dioxide, terpenes, vegetable oils, and carbohydrates are being applied in manufacturing various sustainable materials and products, such as elastomers, plastics, hydrogels, flexible electronics, resins, engineering polymers, and composites [11, 12]. There are large opportunities to apply such sustainable polymers for the manufacture of both high-value fuels and chemicals, and for basic applications like packaging. It is worth noting that effective catalysis is usually demanded to generate monomers, to facilitate selective polymerizations and to enable recycling or upcycling of waste materials [13–15].

The increasing demands of biofuels and fuel additives, among which biodiesel has caused a considerable surplus of glycerol to the market that will create new threats in terms of their sustainable exploitation [16–19]. Stoichiometrically (Scheme 1), for the transesterification of triglycerides with methanol into biodiesel and glycerol, each tonne of biodiesel along with 100 kg of by-product crude glycerol are simultaneously generated [20, 21]. It is important to recognize that the surplus of glycerol will not only arouse the serious disposal issues but also bring about the negative impact on the economy of the biodiesel industry. Therefore, with respect to the biodiesel process, the demand to use such a glycerol fraction by an economical approach is highly desirable [22–25]. A vast majority of means for the incorporation of by-product glycerol into the various branches of industry usually require costly and complicated purification courses. Among the possibilities, glycerol related polymer chemistry and technology has been bringing about increasing concerns because of the diversity of polymer constitutions and architectures available. This branch of industry is one of the largest glycerol consumers after food, pharmaceutical, and personal care applications sectors, and possibly the largest branch with no requirement of complex purification of glycerol during the biodiesel manufacture process [26, 27].

Glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane, GC), a very versatile chemical compound, is a colorless protic polar liquid having the merits of nontoxic, low evaporation rate, low flammability, and high boiling point [28, 29]. It is of great industrial interest to develop the novel approaches to produce GC from glycerol since GC demonstrates the large potential ability in numerous applications, such as reactive protic solvent, surfactants, and pharmaceuticals. More importantly, GC can also serve as the vital building block to prepare polymers, such as polycarbonates, polyglycerol esters, hyperbranched polyols, and nonisocyanate polyurethanes [30, 31].

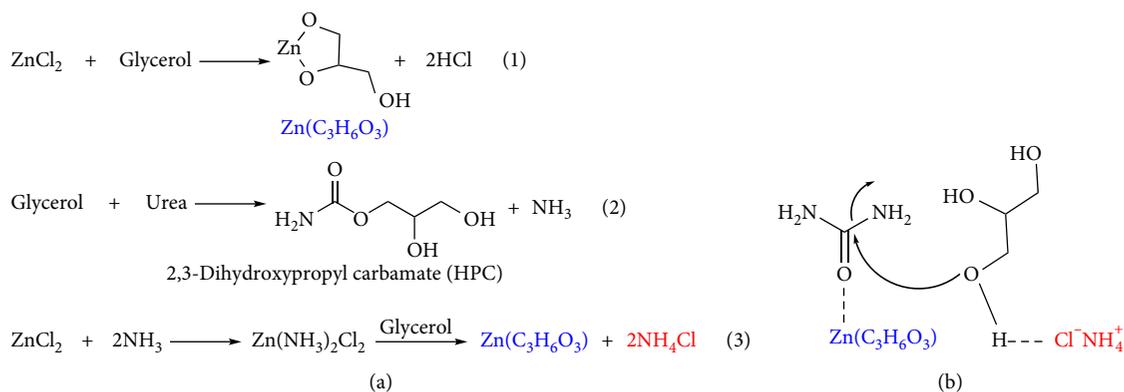


SCHEME 2: Synthetic routes to glycerol carbonate.



SCHEME 3: The glycerolysis of glycerol with urea into glycerol carbonate.

Thus far, some promising manners have been reported for GC manufacture from glycerol, as depicted in Scheme 2: (A) the reaction of glycerol with phosgene; (B) the transesterification of dialkyl carbonates with glycerol; (C) the glycerolysis of urea; (D) the transesterification of ethylene carbonate with glycerol; (E) the direct carboxylation with  $\text{CO}_2$ ; and (F) the oxidative carbonylation of glycerol with  $\text{CO}$  and  $\text{O}_2$  [32, 33]. Nonetheless, upon using ethylene carbonate, GC will be hard to acquire since the by-product ethylene glycol is very difficult to be separated. Moreover, the important environmentally friendly issues should also be considered because the carcinogenic,



SCHEME 4: (a) Reaction routes for the synthesis of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ ; (b) Activation of urea and glycerol by  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$ , respectively.

acutely toxic, and highly flammable substance, oxirane is utilized to prepare ethylene carbonate [34, 35]. Considering the sustainable development, the application of toxic reagents including asphosgene or CO to make GC is also certainly not preferable [36]. In addition, some other attempts to synthesize GC directly using glycerol and  $\text{CO}_2$  under a supercritical reaction condition usually exhibit the low product yields (i.e., zeolites, 8% yield) [37]. Satisfactorily, in comparison with the methods mentioned above, the glycerolysis of urea can be deemed as a relatively green process to produce GC. The main advantages of glycerolysis of urea are that both glycerol and urea are readily available, cheap, and nontoxic, and this simple procedure can be conducted without using any solvent along with the high selectivity and GC yield under mild reaction conditions [38, 39]. It is noteworthy that the GC production from glycerol and urea is currently drawing a mass of attention from a sustainable chemistry perspective: (a) utilizing and reducing the undesirable  $\text{CO}_2$  via the chemical transformation, (b) using the biodiesel by-product glycerol, and (c) producing a value-added chemical GC with versatile practical applications [40, 41]. More importantly, as illustrated in Scheme 3, urea is an easily available and cheap substrate, while the coproduct ammonia, can be cycled back into urea manufacture, rendering the protocol quite atom economical [42].

Therefore, this review is dedicated to the state-of-the-art accomplishments made in the efficient transformation of bio-glycerol and urea into GC. The emphasis would be given to the catalytic performance of the relevant catalysts such as zinc, magnesium, tungsten, ionic liquid-based catalysts, and waste-derived materials, reaction conditions, and possible pathways. In addition, how to modify the reaction conditions that will influence the related activities and selectivity to GC is also depicted.

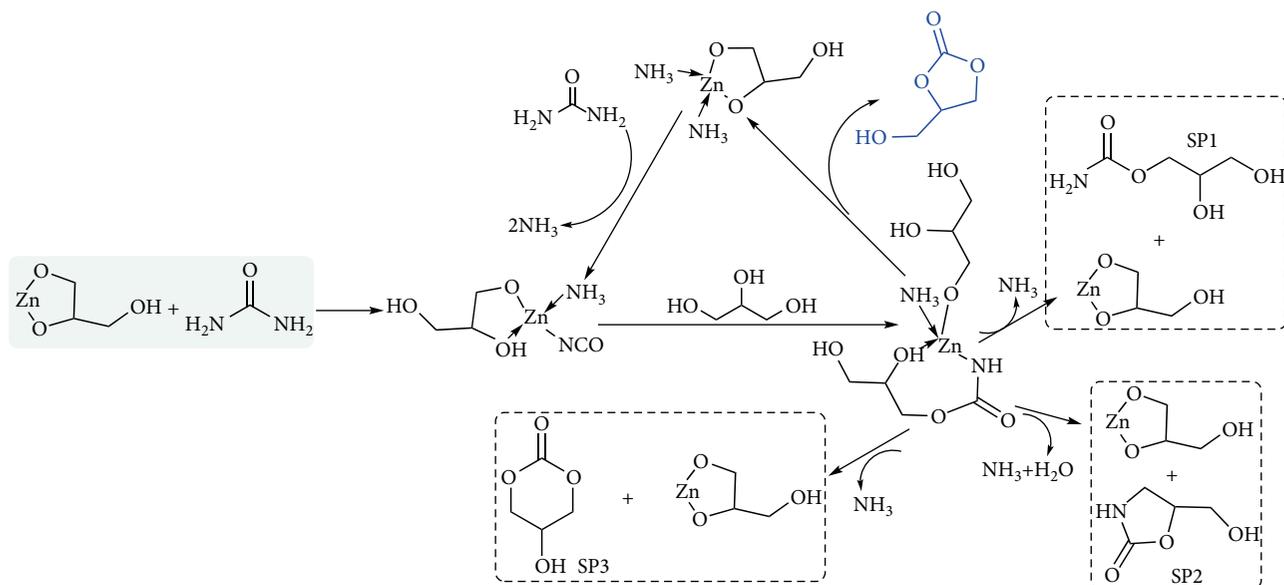
## 2. Catalysts for Glycerol Carbonate Synthesis from Glycerol and Urea

**2.1. Reaction with Zinc-Based Catalyst.** As depicted in Table 1, zinc-based catalysts demonstrate a lot of important results for GC synthesis. Zinc-catalyzed (homogeneous  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  $\text{ZnF}_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ) synthesis of GC using glycerol and urea as substrates, was

systematically evaluated with medium to excellent GC yields. Of the zinc-based catalysts measured,  $\text{ZnCl}_2$  demonstrated the highest catalytic activity, giving a high GC yield of 80.2% with 99.7% selectivity at  $150^\circ\text{C}$  in 2 h along with the urea/glycerol and  $\text{ZnCl}_2$ /glycerol molar ratios of 1 and 0.02, respectively [43]. As shown in Scheme 4(a), according to the spectroscopic and elemental analyses,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  was produced firstly by the reaction of  $\text{ZnCl}_2$  with  $\text{NH}_3$ , followed by reacting with glycerol to transform into zinc glycerolate,  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ , and  $\text{NH}_4\text{Cl}$ . However, the catalytic performance of the sole  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  was determined to be considerably inferior to that of  $\text{ZnCl}_2$ . Upon combining the employment of  $\text{NH}_4\text{Cl}$ , the activity could be greatly enhanced, indicating that the key catalytic active sites for glycerolysis of glycerol with urea were  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$  together. As depicted in Scheme 4(b),  $\text{NH}_4\text{Cl}$  functioned to activate glycerol whereas  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  played the role in activating urea.

The homogeneous catalysts, polymeric glycerolate complexes of zinc (ZMG) and cobalt (CMG) containing a coordinated isocyanate ligand were successfully developed for the production of GC from the mixtures of glycerol and urea [44]. By analyzing the parameters of reaction temperature, time, and glycerol to urea molar ratios, the optimized reaction conditions for achieving a high GC yield of 83% were 5 wt% ZMG catalyst dosage referred to glycerol at  $140^\circ\text{C}$  for 7 h, and glycerol to urea molar ratio of 1:1.5. More importantly, as illustrated in Scheme 5, the proposed reaction mechanism shows that the polymeric glycerolate structure firstly breaks down by the reaction with urea, affording the vital intermediate complex involving a coordinated isocyanate complex. Then, the rearrangement of intermediate isocyanate ligand would generate a carbamate derivative which in turn could reversibly be replaced through cyclizing glycerol into GC. Meanwhile, this would also regenerate the metal monoglycerolate catalyst and the release of ammonia gas under vacuum conditions, accordingly.

By a coprecipitation manner at room temperature, zinc-aluminum hydrotalcite-like composite ( $\text{Zn-Al-SO}_4$ ), comprising sulfate anion with a molar ratio of 3, was developed and employed for preparing GC in one-pot [45]. To determine the optimal parameters, the effects of reaction temperature, time, the molar ratio of glycerol to urea, and dosage of catalyst were investigated in detail. It was found that the synthesis of

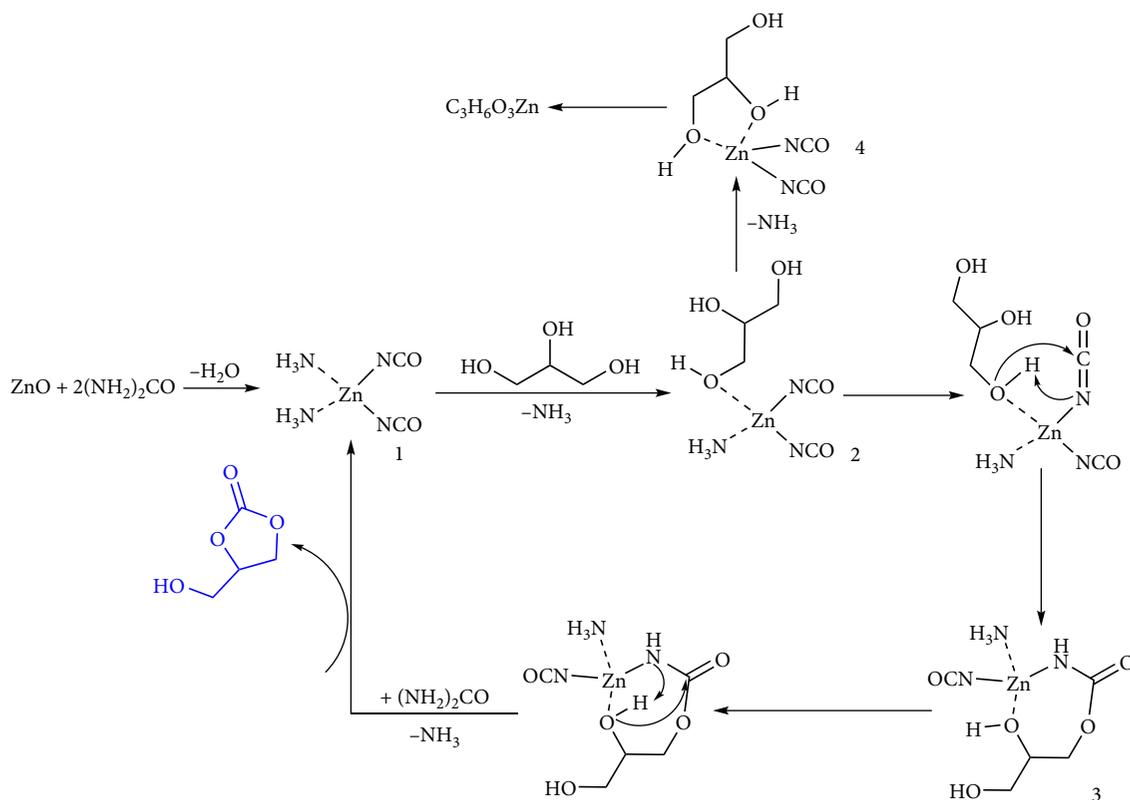


SCHEME 5: Reaction mechanism of glycerolysis of glycerol and urea using ZMG catalyst.

GC could be better conducted using the heterogeneous catalysts bearing an appropriate acidity. Accordingly, the maximum GC yield (92.8%) was determined at 140°C for 4 h using the Zn-Al-SO<sub>4</sub> catalysts with an amount ratio of 3.5 wt%, and 5 wt% stoichiometric excess of urea. Furthermore, the as-prepared catalytic material was found to be insoluble in both the reactants and GC product, wherein enables Zn-Al-SO<sub>4</sub> catalysts to substitute the difficult commercial ZnO or ZnSO<sub>4</sub> catalysts of nonreusable property, to some extent. Interestingly, by deeply investigating the Zn-containing solid catalysts (zinc oxide, smectite, hydrotalcite) along with several inorganic zinc salts for GC synthesis from glycerol and urea proceeded under solvent-free reaction conditions at 130°C, the homogeneous but not heterogeneous catalytic behavior was discovered [46]. The constituent Zn species was found to be dissolved into the liquid phase even for the solid catalysts because of the action of both glycerol and urea, and the GC yield was determined to be correlated with the amount of zinc species leached into the liquid phase with a single relationship. As depicted in Scheme 6, based on the consequences of the reactions carried out under different reaction conditions and the detection of the liquid phase after the reaction by Fourier transform infrared spectroscopy (FT-IR), the possibly active Zn species were determined to be a complex of a Zn atom coordinated with N=C=O. In fact, derived from this study, the dissolved Zn species were the active sites for the glycerolysis of glycerol and urea, which have the same structure irrespective of the parent solid catalysts employed.

To further develop the environmentally friendly catalytic protocols for GC synthesis from glycerol and urea, heterogeneous catalysts of environmental value synthesized by an important preparation stratagem should be considered first and foremost. Motivated by the residue-free and solvent-free synthetic manner that can fabricate the hierarchical nano-scaled catalyst dispersed on microparticles [47–51], the hierarchical nano-scaled Co<sub>3</sub>O<sub>4</sub>/ZnO composites wherein CoO

(40–50 nm) were hierarchically dispersed on the ZnO microscale particles (0.2–1 μm) were synthesized by a very fast, easy and eco-friendly (no solvent, no surfactant, no residue) dry nanodispersion procedure. Importantly, this room-temperature-prepared material could bring about a clear interaction between Co<sub>3</sub>O<sub>4</sub> and ZnO oxides, endowing an excellent catalytic activity (69% conversion and close to 100% selectivity) in the transformation of sustainable resources as the glycerolysis of glycerol with urea at mild condition (140°C for 4 h) [52]. More importantly, Raman spectroscopy evidenced the essence of the interphase oxides reaction whereas the formation of the spinel phase, ZnCo<sub>2</sub>O<sub>4</sub>, upon thermal treated at a high temperature of 400°C was the active species. A novel porous ZnO was manufactured by the calcination method using Zn glycerolate platelets as raw materials which were derived from a glycerol approach, and was used for GC production via glycerol carbonylation with urea [53]. Interestingly, the as-prepared catalyst displayed a porous and irregular morphology along with a proper acid-base property, thus affording the highest GC yield of 85.97% under the optimized reaction conditions of 5.0 wt% catalyst amount, 1:1.5 molar ratio of glycerol to urea at 140°C within 6 h. Interestingly, in contrast to [46], the porous ZnO was also found to maintain its original catalytic performance during 5 recycles, indicating its active, recyclable, and environmentally friendly nature in industrial settings. Zn-Al mixed oxides were synthesized through the coprecipitation or the hydrothermal manner and were employed for GC production by glycerolysis of glycerol with urea [54]. According to the physicochemical property investigated, the coprecipitation-prepared Zn-Al mixed-oxides exhibited the better catalytic performance for GC synthesis than that of the hydrothermal-prepared ones. However, Shin et al. made three important contributions to ZnAl mixed oxides used in synthesizing GC from glycerol and urea, especially focusing on the detailed structure-function relationships [55–57]. ZnO and ZnAl mixed oxides (ZnAlO) were

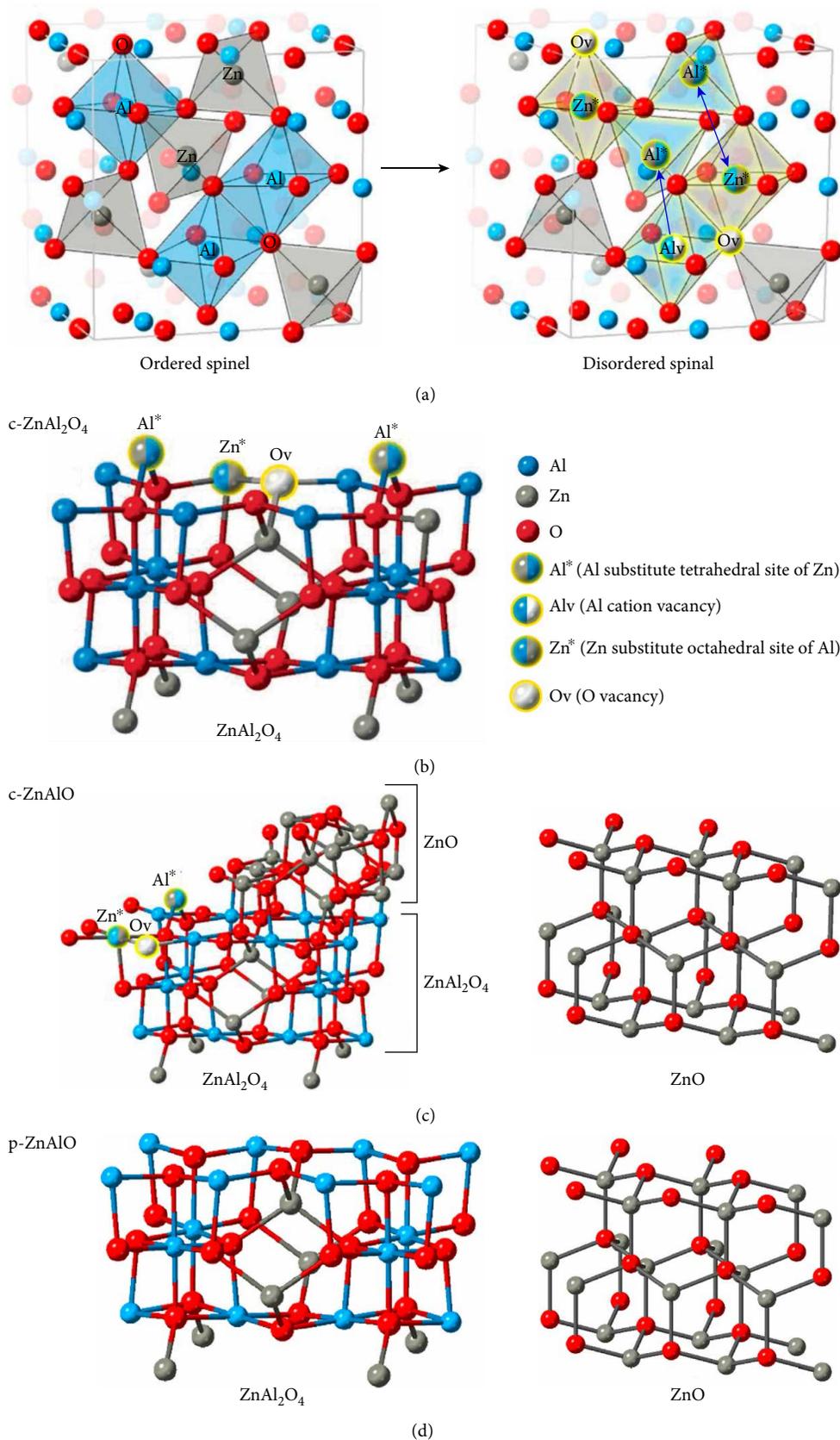


SCHEME 6: The possible reaction mechanism for GC synthesis from glycerol and urea using Zn-containing catalyst.

developed and used in glycerol carbonylation with urea, aiming to investigate the Zn-phase-dependent catalysis in detail [56]. It was found that the ZnAlO catalyst showed higher selectivity and yield of GC than those of ZnO catalyst. In detail, due to the reaction between Zn NCO complex and glycerol, the formed zinc glycerolate (ZnGly) in the solid phase lowered the GC selectivity accordingly. Alternatively, by using the ZnAlO catalyst, the Zn isocyanate (NCO) complexes formed were dominant up to 2 h in both liquid and solid phases. For recent research, they continued to investigate the effect of the disordered  $\text{ZnAl}_2\text{O}_4$  spinel structure on GC production from glycerol and urea using pure  $\text{ZnAl}_2\text{O}_4$  (c- $\text{ZnAl}_2\text{O}_4$ ), ZnAl mixed oxides (c- $\text{ZnAlO}$ ) synthesized by a citrate complex manner, and ZnAl physically mixed oxides (p- $\text{ZnAlO}$ ) [57]. As demonstrated in detail in Scheme 7, the disordered bulk  $\text{ZnAl}_2\text{O}_4$  phase could generate the disordered sites on the catalysts surface:  $\text{Zn}^{2+}$  cations were substituted by  $\text{Al}^{3+}$  cations at the tetrahedral sites, and the surface oxygen vacancy corresponding to the  $\text{Zn}^{2+}$  cations substituting for  $\text{Al}^{3+}$  cations at the octahedral sites. Accordingly, the disordered sites of  $\text{AlO}_4$  and oxygen vacancy of the partially inverted  $\text{ZnAl}_2\text{O}_4$  spinel structure produced high surface acidity for c- $\text{ZnAlO}$  and c- $\text{ZnAl}_2\text{O}_4$ . c- $\text{ZnAlO}$  showed the best catalytic activity because of the higher ability to absorb the liquid Zn NCO complexes. Based on these reports, the solid Zn NCO complex was determined to primarily generate GC, whereas the liquid Zn NCO complex generated both GC and ZnGly.

It is worth mentioning that the acid–base nature of heterogeneous catalytic materials and their surface areas play a

decisive role in GC production efficiency [58, 59]. With respect to this, the novel zinc–tin composite oxide was prepared using three different means including coprecipitation, solid-state, and evaporation methods, and investigated in producing GC [60]. According to the relevant characterization techniques, three components of  $\text{Zn}_2\text{SnO}_4$ , ZnO, and  $\text{SnO}_2$  were determined as the main composite oxides. Upon testing in the selective transformation of glycerol and urea into GC, Zn–Sn mixed oxides synthesized by the coprecipitation manner (ZnSn-CoPre) performed better when compared to the others. Basically, the superior excellent catalytic performance of ZnSn-CoPre should be principally attributed to the existence of higher contents of acid and base active sites. Accordingly, the Zn/Sn molar ratio of 2:1 calcined at  $600^\circ\text{C}$  showed a high 96.0% glycerol conversion and 99.6% selectivity towards GC at  $155^\circ\text{C}$  for 4 h. More importantly, the negligible marginal decrease in catalytic activity was also found when recycled for four times. Moreover, it is anticipated that the combinations of porous structures and metal oxides could potentially endow a better catalytic activity [33, 61]. Interestingly, by using an ingenious heterometallic metal-organic framework (MOF)-templated preparation method of chemical transformation at  $350^\circ\text{C}$ , the highly porous nanocage composite consisting well-joined  $\text{Co}_3\text{O}_4$  and ZnO nanocrystal was triumphantly manufactured and used for GC synthesis from glycerol and urea [62]. Consequently, the as-prepared  $\text{Co}_{50}\text{Zn}_{50}$ -350 catalyst showed a significantly improved catalytic activity in terms of the high yield of GC over 85.2% and 91% GC selectivity, which were superior to those of most solid catalysts. The excellent catalyst



SCHEME 7: Lattice structure of (a) ordered and disordered spinel ZnAl<sub>2</sub>O<sub>4</sub> phase, (b) c-ZnAl<sub>2</sub>O<sub>4</sub>, (c) c-ZnAlO, and (d) p-ZnAlO [57]. Reproduced from Ref. [57] with permission, Copyright 2019 Elsevier.

TABLE 1: Catalytic glycerolysis of urea to GC using zinc-based catalyst.

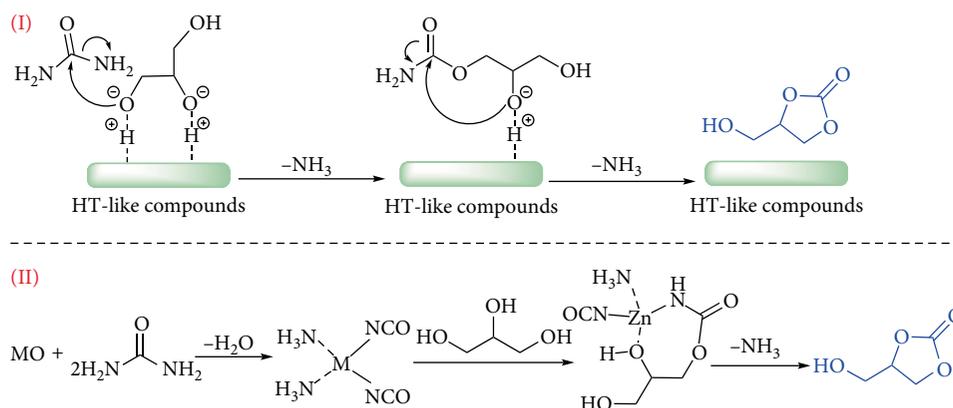
Entry	Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Reaction conditions	Yield of GC (%)	Ref.
1	ZnCl <sub>2</sub>	- <sup>a</sup>	- <sup>a</sup>	150°C, 2 h	80.2	[43]
2	ZMG	- <sup>a</sup>	- <sup>a</sup>	140°C, 7 h	83	[44]
3	Zn-Al-SO <sub>4</sub>	1.58	- <sup>a</sup>	140°C, 4 h	92.8	[45]
4	HT(Zn/Al)	- <sup>a</sup>	- <sup>a</sup>	130°C, 3 h	65.6	[46]
5	Co <sub>3</sub> O <sub>4</sub> /ZnO	- <sup>a</sup>	- <sup>a</sup>	140°C, 4 h	69	[52]
6	Porous ZnO	Integrated area, 5414	Integrated area, 4042	140°C, 6 h	85.97	[53]
7	Zn-Al-O	3.43	2.76	160°C, 5 h	82.4	[54]
8	Zn <sub>6</sub> Al <sub>4</sub>	0.342	0.274	140°C, 3 h	73	[55]
9	ZnAlO	0.375	0.383	140°C, 3 h	68	[56]
10	ZnAl <sub>2</sub> O <sub>4</sub>	0.687	0.287	140°C, 3 h	58	[57]
11	ZnSn-CoPre	0.268	0.061	155°C, 4 h	95.6	[60]
12	Co <sub>50</sub> Zn <sub>50</sub> -350	- <sup>a</sup>	- <sup>a</sup>	150°C, 3 h	85.2	[62]
13	Zn/MCM-41(im)	0.02054	1.61776	145°C, 5 h	73.5	[63]
14	5% Zn/MCM-41	0.5254	0.6177	140°C, 5 h	83	[64]
15	Zn-HY-3	2.64	- <sup>a</sup>	150°C, 3 h	93	[65]
16	Zn <sub>1</sub> TPA	2.677	- <sup>a</sup>	140°C, 4 h	68.8	[66]
17	ZnSO <sub>4</sub>	- <sup>a</sup>	- <sup>a</sup>	150°C, 100 min, micro-wave irradiation (600 W)	93.7	[81]

<sup>a</sup>Not reported.

performance should be attributed to (a) the abundant active species and remarkable mass transfer of the substrates afforded by the as-synthesized nanocages containing massive pores and (2) the more efficient catalytic roles derived from the establishment of Co<sub>3</sub>O<sub>4</sub>/ZnO hetero-interfaces. Unfortunately, the relevant recyclability was not presented.

As mentioned above, the immobilization of active zinc sites onto porous carriers is of significance for achieving high GC yield. With regard to this, Zn impregnated onto mesoporous MCM-41 support catalyst, Zn/MCM-41(im), was successfully developed and investigated the acid-base sites' roles on GC yield in detail [63]. Thanks to its high surface area of 692 m<sup>2</sup> g<sup>-1</sup>, well-dispersed ZnO phase onto the mesoporous framework of MCM-41, and good balanced acid (which activates urea molecules, 0.020 mmol g<sup>-1</sup>) with basic sites (which activates the glycerol, 1.61 mmol g<sup>-1</sup>), 75% glycerol conversion and 98% selectivity of GC were determined. Similarly, immobilizing ZnO catalyst onto the different acid carriers (MCM-41, SBA-15, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and s-ZrO<sub>2</sub>) (5% Zn/MCM-41, 83% GC yield at 140°C in 5 h) [64], Zn-exchanged zeolites including Zn-MOR, Zn-ZSM-5, Zn-beta, and Zn-FAU (Zn-HY-3, 93% GC yield at 150°C for 3 h) [65], activated red mud-supported Zn/Al oxide catalysts (50% Zn/Al-ARM, 58.1% GC yield at 140°C within 5 h) were also reported for efficient transformation of glycerol and urea into GC with relative good yields. Zinc exchanged heteropoly tungstate (Zn<sub>x</sub>TPA) catalysts were successfully developed and evaluated for selective carbonylation of glycerol with urea to manufacture GC [66]. It was determined that the catalytic performance of Zn<sub>x</sub>TPA was mainly decided by the exchangeable Zn<sup>2+</sup> ions that were loaded in the secondary structure of heteropoly tungstate. Exchange of protons of TPA with Zn<sup>2+</sup> ions could generate acid Lewis and Bronsted sites, simultaneously. Under the reaction temperature of 140°C and reaction time of 4 h, 68.8% GC yield was achieved by using Zn<sub>1</sub>TPA catalyst.

Normally, the glycerolysis of urea has to be operated under a vacuum condition or a sweeping gas to eliminate the by-product ammonia, to shift the chemical equilibrium towards the products [67]. Moreover, to our knowledge, previous works on the glycerolysis of urea have been performed in batch operation making it difficult to be applied to industrial-scale [40, 68, 69]. Therefore, it is of high importance to develop a new procedure to prepare GC through the carbonylation of glycerol with urea at atmospheric pressure and continuous operation. With the aim of reducing the by-product NH<sub>3</sub> that shifts the thermodynamic chemical equilibrium, the combing of the reaction and separation units in a single reactive distillation column process was developed accordingly [70]. Through this promising process of reactive distillation, the optimal design and operating variables for GC production were no rectifying stage, 3 reactive stage, 3 stripping stages, reflux ratio of 2, and reboiler heat duty of 15 kW for each glycerol and urea feed flow rate of 100 mol/h, giving a high 90.0% GC yield and 100% purity of GC. Moreover, compared to the traditional *in vacuo* manner, reactive distillation improved the glycerol conversion of 29.1% and saved in energy consumption by 37.1%, accordingly. Importantly, the interesting microwave irradiation technology has been developed and employed in various procedures, like chemical reaction [71, 72], material synthesis [73], nanotechnology [74] and biochemical processes [75, 76]. It is noteworthy that microwave would improve the product yield and shorten the reaction time in producing carbonates from CO<sub>2</sub> and epoxide [77], NaHCO<sub>3</sub> and olefins [78], CO and diols [79], and polycarbonates from open-ring polymerization of trimethylene carbonate [80]. Han et al. performed important research in the synthesis of GC from glycerol and urea with and without the microwave irradiation condition [81]. By using ZnSO<sub>4</sub> as the catalyst, the glycerolysis reaction could efficiently proceed with the assistance of microwave, and the high GC yield reached



SCHEME 8: Proposed mechanism for GC production from glycerol and urea using HT.

TABLE 2: Catalytic glycerolysis of urea to GC using magnesium-based catalyst.

Entry	Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Reaction conditions	Yield of GC (%)	Ref.
1	MgO	- <sup>a</sup>	- <sup>a</sup>	140°C, 5 h	70 <sup>b</sup>	[82]
2	Combustion synthesized MgO	0.69	0.73	150 °C, 6 h	71	[91]
3	2.5 wt% Au-MgO	- <sup>a</sup>	- <sup>a</sup>	150°C, 4 h	73	[95]
4	Au-Pd-MgO	- <sup>a</sup>	- <sup>a</sup>	150°C, 4 h	67	[96]
5	HT(Mg/Zn/Al)	- <sup>a</sup>	- <sup>a</sup>	130°C, 3 h	83.7	[97]
6	Mg-Al-Zr	0.119	0.261	140°C, 3 h	87.8	[98]

<sup>a</sup>Not reported. <sup>b</sup>Glycerol conversion.

93.7%. It could be believed that this green and effective process will show a promising prospect in GC production application.

**2.2. Reaction with Magnesium-Based Catalyst.** As shown in Table 2, magnesium-based catalysts also perform well in GC production from glycerol and urea. Three catalysts involving ZnO/Zeolite, PbO/Zeolite, and MgO were investigated for biodiesel synthesis from *Jatropha* oil, and the highest biodiesel yield using ZnO/zeolite reached 93.8 %. However, for the utilization of biodiesel byproduct glycerol, MgO as a catalyst was found to perform better than ZnO for the production of GC via urea-glycerol [82]. Nearly 70% glycerol conversion for MgO at 140°C within 5 h could be presented, which was higher than that of ZnO with 60% glycerol conversion. Generally, various protocols for the manufacture of nanocrystalline metal oxides such as inert gas condensation, laser ablation, chemical vapor deposition, sputtering, molecular beam epitaxy, coprecipitation [83], sol-gel process [84], thermal decomposition of nitrates and carbonates [85], and combustion synthesis [86–90] have been reported. Particularly, combustion synthesis was proven to improve the activity, shape selectivity, and to generate more active sites for acid and base catalysts. An eco-friendly manner has been reported in the selective conversion of glycerol and urea to GC using MgO that was prepared by the combustion method with glycerol as fuel [91]. Up to 71% glycerol conversion with 100% selectivity was determined by using the as-prepared MgO catalyst at 150°C for 6 h. In addition, the recoverable and reusable characters of the MgO catalyst during the consecutive reactions could also be found.

Gold (Au) has attracted great attention because of its catalytic activity serving as the homogeneous and heterogeneous catalysis [92]. Especially, gold was proven to perform well in the selective oxidize glycerol to glyceric acid in aqueous solution [93], and selective solvent-free oxidation of alcohols [94]. More importantly, gold could also serve as an active Lewis acidic catalyst upon being suitably immobilized on the advisable oxides. Therefore, it is of great interest to design the supported gold catalyst for GC synthesis from glycerol and urea. By using a simple impregnation method, the Au immobilized on the supports of titania, carbon, niobium oxide, zinc oxide, and magnesium oxide was successfully developed and tested in GC synthesis [95]. It was reported that the most active catalyst was the 2.5 wt% Au deposited on MgO followed by calcined at 400°C, showing 73% yield of GC at 150°C which were superior to that of homogenous zinc sulfate salts. As evidenced in this report, the promotion of the intramolecular cyclization of the carbamate intermediate to generate GC was the key role. More importantly, the catalyst could maintain its catalytic reactivity even after 10 recycles. After this research, bimetallic gold and palladium nanoparticles were further supported on MgO and utilized as the efficient catalytic material in promoting the synthesis of GC using urea and glycerol as feedstocks [96]. Through both of the sol immobilization and impregnation manners, high dispersions of the vibrant metals could be obtained. Interestingly, the MgO partly underwent transformations into magnesium carbonate upon reaction since the little impact on reactivity was found.

The Mg-Al hydrotalcite catalyst was investigated in GC production, and the hydrotalcite-like compounds containing Mg, Zn, and Al metals showed an excellent catalytic performance [97]. Consequently, 89.8% conversion of glycerol and 93.2% selectivity for GC were presented under 130°C for 3 h by using HT(Mg/Zn/Al) catalyst. Furthermore, the proposed reaction mechanism realized with two routes promoted by hydrotalcite-like compounds is depicted in Scheme 8. As reported in this research, Route I was deemed as the possible heterogeneous mechanism. Firstly, a bidentate ligand was formed through the coordination of glycerol with HT *via* hydrogen bond, wherein the oxygen atoms would be activated. The oxygen of the primary alcohol attacked the carbonyl carbon of urea that might generate NH<sub>3</sub>. Afterward, the oxygen of the secondary hydroxyl group further attacked the carbonyl carbon through the intramolecular transesterification, which is supported because of the stable five-member cycle structure. The second NH<sub>3</sub> was also produced and GC would be detached from the surface of HT. Route II should be a plausible homogeneous mechanism. Initially, the metal complex was generated, wherein the two NH<sub>3</sub> from urea were weakly coordinated. Then, one of the coordinated NH<sub>3</sub> was exchanged with glycerol, leading to the intermediate to which glycerol interacted with the metal centers by their oxygen. Followed by this, the interacting hydroxyl groups of glycerol captured the adjacent isocyanate groups. Finally, the coordinated carbamate groups would be converted into GC by intracyclization, releasing NH<sub>3</sub> and the catalytic active ingredients. After that, a sequence of Mg-Al hydrotalcite-like (HTL) catalysts doped with Zr bearing the mesoporous structures upon under heat treatment were also developed and employed for GC production from glycerol and urea [98]. As a result, the well-balanced surface acid and base active sites of the catalyst with  $Zr^{4+}:(Al^{3+} + Zr^{4+}) = 0.3$  demonstrated the highest 87.8% yield of GC at 140°C within 3 h.

**2.3. Reaction with Tungsten-Based Catalyst.** In Table 3, tungsten-based catalysts also show interesting works regarding GC synthesis. A series of tungsten (W)-tin (Sn) mixed oxides with varied mole ratios were synthesized using the coprecipitation process and evaluated for GC production from glycerol and urea [99]. Sn-W catalyst with a 2:1 molar ratio calcined at 500°C showed the best catalytic performance in terms of 52% of glycerol conversion with >95% GC selectivity. Similarly, different WO<sub>3</sub> contents supported on SnO<sub>2</sub> catalytic materials were prepared and employed for GC synthesis [100]. *In situ* Raman technology revealed the existence of isolated monomers and polymeric species of WO<sub>3</sub>. Accordingly, the glycerol conversion and selectivity were found to be depended on the well-dispersed amorphous WO<sub>3</sub> which in turn was related to the acidity of the catalysts. The catalyst with 5 wt% WO<sub>3</sub> on SnO<sub>2</sub> calcined at 500°C for 4 h brought about the high dispersions of larger contents of strong acid active sites, giving 85.4% selectivity towards GC at 140°C in 4 h. Following up these valuable studies, tungsten oxide species supported on titania catalysts (100% selectivity for GC, 140°C in 4 h) [101], silicotungstates impregnated into MCM-41 (77% selectivity for GC, 150°C in 8 h) [102], silicotungstates anchored to large

pore zeolite H $\beta$  (75% selectivity for GC, 150°C in 8 h) [103] were also developed for GC synthesis with authentic and acceptable results.

Early transition metals formed in the metal-oxygen clusters of their highest oxidation state, also known as polyoxometalates (HPA), are a group of important inorganic compounds showing large potential application prospects in catalysis [104–106]. Due to their compelling features of strong Brønsted acidity, multistage redox activity, and remarkable thermal and hydrolytic stability, polyoxometalates have been applied in acid and oxidation catalysis. In addition, the catalytic properties can be tuned by proton exchange of the HPA with various metal or alkali ions. For instance, the proton exchange of tungstophosphoric acid with Cs<sup>+</sup> generated a strong acid in comparison with the pristine acid [107]. In a similar manner, exchanging the protons of the HPA with Sn<sup>2+</sup> and Al<sup>3+</sup> resulted in the Lewis acidic sites [108–110]. In this context, samarium-exchanged heteropoly tungstate catalyst (Sm<sub>x</sub>TPA) was designed and used for GC synthesis, aiming to enhance the acidity thereby increasing GC yield accordingly [111]. The activity of the catalysts was determined to depend on the Lewis and Brønsted acidity that came from the Sm contents, and the partially exchanged Sm<sub>x</sub>TPA catalysts exhibited the best performance, due to the higher amounts of Lewis acid sites. As illustrated in Scheme 9, the plausible reaction mechanism using Sm<sub>x</sub>TPA catalysts was also proposed by the authors. In short, Lewis and Brønsted acidic sites activated the carbonyl group of urea, the conjugate base, and the hydroxyl group of the glycerol. Cs-exchanged heteropolyacid catalysts functionalized with Sn, Sn-CsPW (83% GC selectivity, 140°C) [112], tantalum exchanged tungstophosphoric acid catalysts (100% GC selectivity, 140°C) [113] were also developed for GC synthesis from glycerol and urea.

**2.4. Reaction with Functional Ionic Liquid.** Using ionic liquids (ILs) as catalysts to produce GC via urea-glycerol is also presented in Table 4. Acidic, basic, and neutral ILs were adopted as the catalysts for GC production through glycerolysis of glycerol with urea [114]. Interestingly, neutral ILs were determined to perform best while acid and base ILs exhibited the poor activity. The well-balanced acid–base properties of the neutral ILs that were derived from the synergistic effect of the cations and anions, were treated as the key role in obtaining high GC yield. The positively charged cation activated urea by attracting the electronegative oxygen of the carbonyl group of urea, which was similar to that of Lewis acid site. On the other hand, the negatively charged anion attracted the proton of glycerol at the same time. Moreover, the IL catalysts could be recycled and reused at least 5 times without significant activity decrease. Nonetheless, the obvious difficulty in separation and recovery will limit ILs to be applied on a large scale [115]. Of particular interest is to immobilize ILs through heterogenization of ILs onto suitable solid supports like organic polymers and inorganic materials [116, 117]. By the reaction of imidazole with alkoxyated Merrifield peptide resin (MPR), ILs incorporated on the MPR catalysts MPR-ILs were successfully developed [118]. MPR-ILs with longer alkyl chains and fewer sterically hindered counteranions demonstrated better catalytic performance in GC synthesis, giving 80.9%

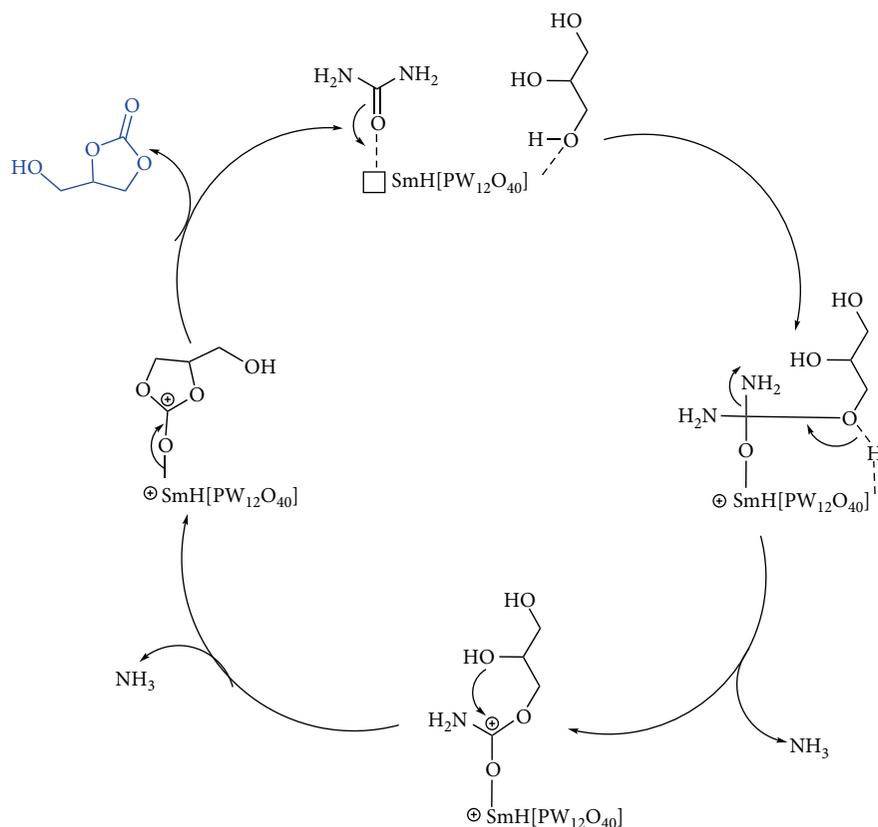
SCHEME 9: Proposed reaction mechanism using Sm<sub>x</sub>TPA catalyst.

TABLE 3: Catalytic glycerolysis of urea to GC using tungsten-based catalyst.

Entry	Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Reaction conditions	Yield of GC (%)	Ref.
1	SW21	0.472	- <sup>a</sup>	140°C, 4 h	49.4	[99]
2	5 wt% WO <sub>3</sub> -SnO <sub>2</sub>	0.271	- <sup>a</sup>	140°C, 4 h	85.4 <sup>b</sup>	[100]
3	15% WO <sub>3</sub> /TiO <sub>2</sub>	0.554	- <sup>a</sup>	140°C, 4 h	73	[101]
4	30% SiW <sub>12</sub> /MCM-41	3.4	- <sup>a</sup>	150°C, 8 h	77 <sup>b</sup>	[102]
5	SiW-Hβ	3.5	- <sup>a</sup>	150°C, 8 h	75 <sup>b</sup>	[103]
6	Sm <sub>0.66</sub> TPA	1.726	- <sup>a</sup>	140°C, 4 h	85 <sup>b</sup>	[111]
7	Sn-CsPW	528	- <sup>a</sup>	140°C, 4 h	85 <sup>b</sup>	[112]
8	Ta <sub>0.4</sub> TPA	0.128	- <sup>a</sup>	140°C, 4 h	100 <sup>b</sup>	[113]

<sup>a</sup>Not reported. <sup>b</sup>GC selectivity.

selectivity of GC at 140°C for 3 h. High temperature, high degree of vacuum and the addition of co-catalyst of ZnO could improve the GC selectivity to 100%.

As depicted in Scheme 10, the Zn-containing ILS immobilized on the polymeric support polystyrene (PS) PS-(Im)<sub>2</sub>ZnBr<sub>2</sub>, was successfully developed and employed for GC production [119]. PS-(Im)<sub>2</sub>ZnBr<sub>2</sub> was prepared through two steps: (1) bis[1-(2-hydroxyethyl)imidazolium]zinc bromide (HEIm)<sub>2</sub>ZnBr<sub>2</sub> was synthesized via metal insertion; (2) the (HEIm)<sub>2</sub>ZnBr<sub>2</sub> was incorporated into MPR by alkoxylation. Under the reaction temperature of 140°C for 6 h, 72.3% selectivity of GC was achieved using (HEIm)<sub>2</sub>ZnBr<sub>2</sub> catalyst because of its well-balanced acid-base properties. In addition, the as-synthesized catalyst could be reused for 4

times with 70.1% selectivity of GC. Various quaternary ammonium salts (QX) ILS supported onto montmorillonite clay (Q-MMT) were manufactured through the ion-exchange method between the tetra-alkyl ammonium salts and ions in the clay interlayer [120]. By the detailed investigations, the Q-MMTs were found to perform well in the selective synthesis of GC from glycerol and urea, showing 80% selectivity of GC at 145°C within 3 h. More importantly, Q-MMT could be easily reused during 4 recycles without any significant activity decrease. Similar to [119], polystyrene immobilized with different kinds (Cu, Mg, Zn) of metal-containing imidazolium salt [PS-(Im)<sub>2</sub>MX<sub>2</sub>] catalysts were prepared and used for GC production [121]. Among different metal-containing PS-(Im)<sub>2</sub>MBr<sub>2</sub> catalytic materials, the yield of GC increased

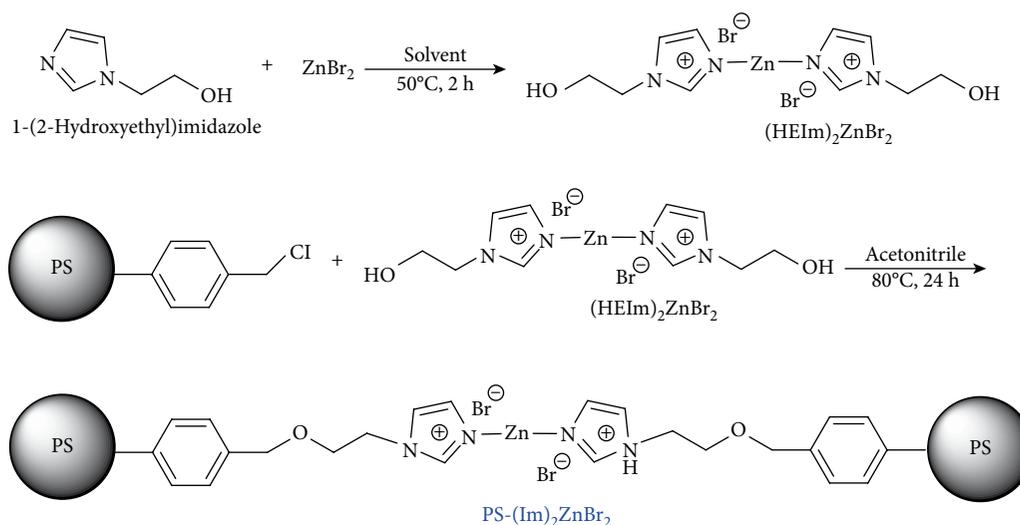
SCHEME 10: The synthetic route for PS-(Im)<sub>2</sub>ZnBr<sub>2</sub>.

TABLE 4: Catalytic glycerolysis of urea to GC using ILS-based catalyst.

Entry	Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Reaction conditions	Yield of GC (%)	Ref.
1	MPR[pmim][Cl] + ZnO	- <sup>a</sup>	- <sup>a</sup>	140°C, 3 h	78.6	[118]
2	PS-(Im) <sub>2</sub> ZnBr <sub>2</sub>	0.165	0.66	140°C, 6 h	72.3 <sup>b</sup>	[119]
3	Q-MMTs	- <sup>a</sup>	0.97	145°C, 3 h	80 <sup>b</sup>	[120]
4	[PS-(Im) <sub>2</sub> MX <sub>2</sub> ]	6.01	6.67	140°C, 6 h	60.3	[121]

<sup>a</sup>Not reported. <sup>b</sup>GC selectivity.

TABLE 5: Catalytic glycerolysis of urea to GC with other catalysts.

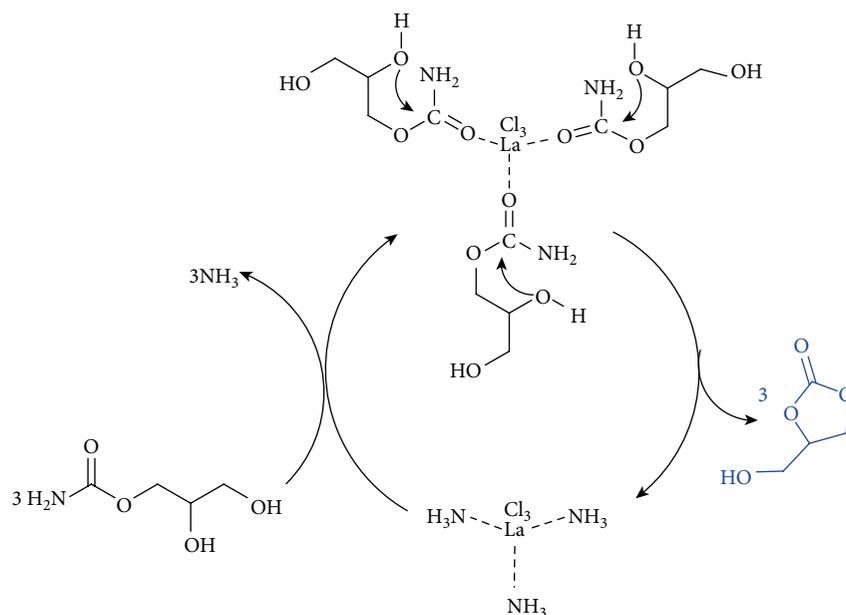
Entry	Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Reaction conditions	Yield of GC (%)	Ref
1	La <sub>2</sub> O <sub>3</sub>	- <sup>a</sup>	0.108	140°C, 1 h	90	[124]
2	La <sub>2</sub> Cu <sub>0.5</sub> Fe <sub>0.5</sub> O <sub>4</sub>	Qualitatively, not quantitatively	Qualitatively, not quantitatively	150°C, 4 h	81.9 <sup>b</sup>	[125]
3	Cu <sup>1</sup> Mn	Qualitatively, not quantitatively	Qualitatively, not quantitatively	140°C, 6 h	99.1 <sup>b</sup>	[126]
4	AlCaMO	Qualitatively, not quantitatively	Qualitatively, not quantitatively	145°C, 5 h	88 <sup>b</sup>	[68]
5	γ-Zirconium phosphate	1.49	0.18	135°C, 3 h	100 <sup>b</sup>	[127]
6	Waste boiler ash	- <sup>a</sup>	7.1	150°C, 4 h	84.3	[128]
7	Gypsum-based catalyst	0.12	- <sup>a</sup>	150°C, 4 h	83.6	[129]

<sup>a</sup>Not reported. <sup>b</sup>GC selectivity.

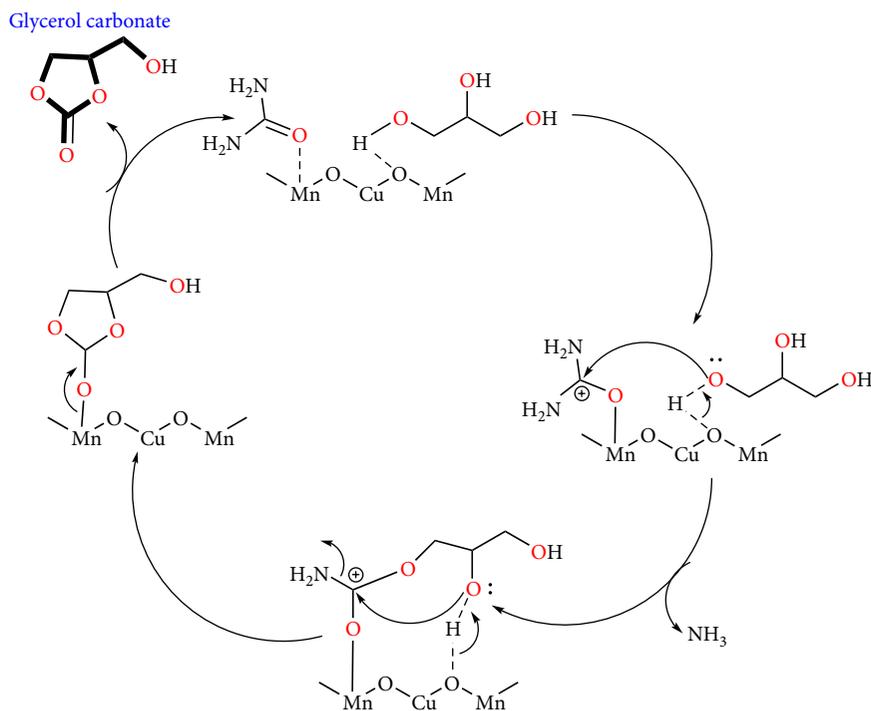
Cu < Mg < Zn, which follows the order of acid-base balance of the catalysts wherein Zn-containing catalyst presented better acid/base ratio than those of Mg and Cu.

**2.5. Reaction with Other Catalysts.** In addition to the catalytic materials mentioned above, some other catalysts illustrated in Table 5 also demonstrate good results for GC production. Commercial polymeric cation resin Amberlyst-15 was used for GC synthesis from urea and glycerol with 62.76% glycerol conversion at 120°C for 5 h [122]. Three lanthanum

(La) based catalysts were also developed in the synthesis of GC, including LaCl<sub>3</sub> [123], La<sub>2</sub>O<sub>3</sub> [124], and La<sub>2</sub>Cu<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> [125]. For LaCl<sub>3</sub> catalyzed glycerolysis, the key reaction mechanism is illustrated in Scheme 11. Three oxygen atoms of the carbonyl group of the 2,3-dihydroxypropyl carbamate (HPC) coordinated with La<sup>3+</sup> of LaCl<sub>3</sub>; the electrons of C–N groups redistributed wherein the proton transferred onto the carbon atom leading to the carbocation and nitrogen anion and favoring the intramolecular nucleophilic attack of adjoining hydroxyl group. Consequently, there was the



SCHEME 11: The proposed reaction mechanism for GC synthesis from HPC over  $\text{LaCl}_3$ .



SCHEME 12: The possible reaction mechanism for the synthesis of GC by Cu-Mn composites.

important bond between the electrophilic carbonyl carbon of complex and the lone pair of electrons of oxygen of the hydroxyl group. Meanwhile, the hydrogen protons broke away from the hydroxyl groups united with the amino groups leaving from the formed complexes. At last, the final product GC was generated by the broke of C-N bond and the new formation of C-O bond, while the corresponding complex  $\text{La}(\text{NH}_3)_3\text{Cl}_3$  could be also regenerated. In addition, due to

the strong nucleophilicity of HPC and the release of  $\text{NH}_3$ , the catalytic circulation was finished accompanied by the substitution of  $\text{NH}_3$  molecules with HPC.

Cu-Mn composite oxides prepared by coprecipitation method (99.1% GC selectivity, 140°C for 6 h) [126], Al/Ca-mixed oxide (AlCaMO) derived from hydrotalcite (88% GC selectivity, 145°C for 5 h) [68],  $\gamma$ -zirconium phosphate (100% GC selectivity, 135°C for 3 h) [127], waste boiler

ash (90.1% GC selectivity, 150°C for 4 h) [128], and gypsum-based catalyst (90.1% GC selectivity, 150°C for 4 h) [129] were developed for GC manufacture. For the GC production catalyzed by Cu–Mn composites (Scheme 12),  $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$  crystal phase was determined as the active species in glycerolysis. It was reported that this phase can efficiently afford acid sites of  $\text{Mn}^{4+}$  and lattice oxygen  $\text{O}^{2-}$  base sites, and the presence of the  $\text{Mn}^{4+}\text{--O}^{2-}$  Lewis acid-base pairs would facilitate the transformation of glycerol and urea into GC, consequently.

### 3. Conclusion

The effective production of glycerol carbonate (GC) has been arousing great attention because of its importance in lessening excessive glycerol in biodiesel process as well as its potential industrial application prospect, especially in the polymer area. Selective catalytic valorization of glycerol with urea by carbonylation into GC has been shown to be the most promising in terms of the reactants available and reaction environmental benefits. Although the sole acidic or basic site can exhibit some reactivity for glycerolysis of urea, the achievement of high conversion and high selectivity of GC using recyclable heterogeneous catalysts remains a great challenge. On the one hand, the strong interaction between urea and acid sites will lead to the deactivation of active sites for further procedures. On the other hand, the undesirable reactions like decarbonylation and 2-HPC dehydration can be accelerated by the base and the GC selectivity will decrease due to the overmuch amounts of basic sites. Consequently, the catalysts with the appropriate balance of active acidic and basic sites will be favorable for the synthesis of GC from glycerol and urea. Moreover, the energetical development of heterogeneous catalysts of high-performance for this process demonstrates the powerful and significant strategic and environmental benefits.

It is noteworthy that the catalytic activity of catalysts can be considerably improved by the rationale regulating their compositions and surface structures. As anticipated, the joint application of pore formation such as well-defined ordered channel frameworks and catalytic active species combinations would potentially enable the promising environmentally friendly catalysts. In addition, insightful reaction mechanisms and structure-property understanding will also help us to design the appropriate catalysts for GC manufacture from glycerol and urea. Finally, the proper employment of the relevant auxiliaries to boost catalytic activity and product selectivities, such as heating modes of microwave irradiation and reactive distillation replacing the traditional in vacuo system are also suggested.

### Conflicts of Interest

The authors have no conflicting interests to declare.

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