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## The value-added utilization of glycerol for synthesis of glycerol carbonate catalyzed with a novel porous ZnO catalyst

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In the carbonation reaction, novel porous ZnO was prepared by calcination method and the raw material Zn glycerolate platelets were prepared via the glycerol approach, which could make use of byproduct glycerol. To elucidate their composition, morphology and properties, the resulting materials were characterized by using: FT-IR, XRD, SEM, BET, XPS, TPD and TG respectively. The results showed that the catalyst with porous and irregularly shaped with appropriate acid and base properties had better catalytic performance to synthesis of glycerol carbonate. The highest glycerol carbonate yield reached 85.97% of ZnO from zinc glycerolate under the optimal reaction conditions: 5.0 wt.% of catalyst adding, 1:1.5 of the molar ratio of glycerol to urea and reacting at 140 °C for 6 h under 1KPa. Compared with three catalysts ZnO, zinc glycerolate and ZnO from zinc glycerolate, the maximum glycerol carbonate yield 85.97% with the ZnO from zinc glycerolate, the maximum glycerol carbonate. Compared with the conventional ZnO, as-prepared catalyst embodied in its porosity, acidity and basicity. The catalyst maintained excellent catalytic performance after 5 cycles, almost no loss of catalytic activity. The study revealed that the ZnO from zinc glycerolate catalyst with high activity, highly recyclable, remarkably stable, and environmental friendly is appropriately applied in industrialization. Overall, this new material overcomes the limitation of glycerol application and would have a good potential for industrial application.

#### 1. Introduction

The sharp increase in demand for fuels and the increase in environmental problems, coupled with reduction of crude oil reserves, have attracted people's attention about renewable energy<sup>1</sup>. Biodiesel as renewable energy has developed very well in recent years<sup>2</sup>. In fact, the production of biodiesel is still relatively far away from the intended target which due to the high cost of production. In order to maintain the balance of the glycerol existing market, improve the added value of glycerol and promote the development of biodiesel industry, many researchers focus on the study of valued-added glycerol derivatives. So the glycerol as biodiesel by-product is the viable method to reduce the cost of biodiesel production<sup>3-5</sup>.

Conversion process of glycerol as a renewable and cheap raw chemical to high value-added products which have attracted more and more people's attention<sup>6</sup>. Glycerol carbonate is a small molecule with a bifunctional compound: dioxolane ring and hydroxyl group<sup>7-8</sup>. The bifunctional compound as reactive sites make glycerol carbonate as a raw material to synthesis chemical intermediates achievable. Glycerol carbonate can react both as a nucleophile through its hydroxyl group, and as an electrophile through its ring carbon atoms. Glycerol carbonate can be used as solvents, beauty & personal care, chemical intermediates, polymers such as hyperbranched polyethers, polycarbonates, polyurathanes and non-isocyanate polyurethanes. Glycerol carbonate have a lot of potential applications in manufacturing useful materials such as carrier in pharmaceutical preparations, carrier in lithium and lithium-ion batteries, solid laundry detergent compositions<sup>9</sup>.

It is carried out to synthesis glycerol carbonate directly from glycerol and subcritical CO<sub>2</sub> using Cu/La<sub>2</sub>O<sub>3</sub><sup>10</sup>, nBu<sub>2</sub>SnO<sup>11</sup>, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>-ZnO<sup>12</sup> catalysts. Glycerol carbonate can be synthesized through the reaction of glycerol with CO and O<sub>2</sub> in the presence of PdCl<sub>2</sub>(phen)/KI catalysts<sup>13</sup>. Glycerol carbonate could be synthesized with several different synthetic routes such as the transesterification reaction of glycerol and dimethyl carbonate or diethyl carbonate using  $K_2CO_3^{14}$ , CaO<sup>15</sup> and hydrotalcite<sup>16</sup> and the carbonylation reaction of glycerol and urea in the presence of catalyst such as metal oxides<sup>17-18</sup>, WO<sub>3</sub>/SnO<sub>2</sub><sup>19</sup>, ionic liquids<sup>20</sup>, lanthanum compounds<sup>21</sup>, gypsum based catalyst<sup>22</sup>, Zn-Al mixed-oxide catalyst<sup>23</sup>, WO<sub>3</sub>/TiO<sub>2</sub><sup>24</sup>, tantalum in henteropoly tungstate catalysts<sup>25</sup>, y-zirconium phosphate<sup>26-28</sup>, calcined Zn hydrotalcite<sup>29</sup>,  $Co_3O_4/ZnO^{30}$ , gypsum and gold-based catalysts<sup>31-32</sup>. CO and phosgene don't meet with the requirements of sustainable development. The use of carbon dioxide as carbonating agent required high temperature and high pressure and the yield for glycerol carbonate was too low for practical purpose.



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In our work, a novel solid catalyst was used for catalyzing glycerol and urea to synthesize the high value-added glycerol carbonate. Attempts are being focused on using urea due to its cheaper cost and safe handling. Furthermore, ammonia formed can be easily converted to urea since the urea synthesis performed from ammonia and carbon dioxide. The performances of three catalysts ZnO, zinc glycerolate and ZnO from zinc glycerolate were compared under optimizing operating conditions. The catalyst was also characterized by FT-IR, XRD, SEM, BET, TPD, XPS and TG. In addition, the combination of a weak Lewis acid and Lewis base was found in the carbonate formation. In the reaction, glycerol can be used not only as the reactant but also as the catalyst precursor.

#### 2. Experimental Section

#### 2.1 Materials

Anhydrous glycerol of high purity (>99%), urea (>99%), absolute ethanol (>99%), acetic acid (99%), zinc nitrate hexahydrate  $Zn(NO_3)_2 \cdot GH_2O$  (99%), zinc acetate dihydrate  $Zn(CH_3COO)_2 \cdot 2H_2O$  (99%), oxalic acid (99%), potassium hydroxide KOH (99%) and zinc chloride (99%) were obtained from Sinopharm Chemical Reagent Co, Ltd, China.

#### 2.2 Catalyst preparation

 $Zn(CH_3COO)_2 \cdot 2H_2O$  (2g) was mixed with glycerol (20g) at 160 °C under reflux for 5h. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 150 °C for 18 h. The product mixture was filtered, washed with distilled water, and dried at 80 °C in air overnight. Then, the obtained white fine powder was Zn glycerolate. The as-prepared samples were labeled as ZMG and was heated with different thermal produres (heating rate). Finally, the synthesized precursor ZMG was decomposed to ZnO by calcination at 450 °C in an N<sub>2</sub> flow for 2 h (heating temperature rate was set to 0.5 °C/min). The optimal thermal method were as follows: 450°C, 0.5 °C/min.

In the 0.5mol/L zinc nitrate solution, potassium hydroxide was added to prepare zinc hydroxide. The synthesized precursor  $Zn(OH)_2$  was decomposed to ZnO by calcination at 450 °C in air for 2 h.

#### 2.3 Catalyst characterization

As to the solid catalyst, 1mg sample and 200mg KBr were ground completely and pressed into thin disks. Subsequently, the FT-IR of sample were tested by FTLA2000 type Fourier transform infrared spectrometer of the Canadian ABB company with scanning range  $4000 \approx 500 \text{ cm}^{-1}$ .

X-ray diffraction (XRD) patterns were examined with a Bruker D8 Advance powder diffractometer using Cu K $\alpha$  radiation source ( $\lambda$ = 1.5406 Å) at 40 kV and 40 mA from 10° to 90° with a scan rate of 4° min<sup>-1</sup>.

The morphology of the catalyst was evaluated by field emission scanning electron microscopy (FE-SEM) on a Hitachi S-4800.

The specific surface area and pore diameter of the catalysts was measured according to the Brunauer-Emmet-Teller (BET) method with nitrogen adsorption-desorption with ASAP 2020 instrument (Micromeritics, USA).

Temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was measured for basicity and base intensity distribution of the catalysts. The sample was pretreated under helium flow 300 °C for 1 h. Subsequently, it was cooled to 50 °C to adsorb CO<sub>2</sub>. After adsorption CO<sub>2</sub> 30min, the catalyst was pretreated under helium flow 100 °C for 1 h to remove the adsorbed CO<sub>2</sub> from sample surface. Desorption curve was recorded from 100 °C to 800 °C at 10 °C /min.

Temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was performed for acidity and acid intensity distribution of the catalysts. The sample was pretreated under helium flow 300 °C for 1 h. Subsequently, it was cooled to 50 °C to adsorb NH<sub>3</sub>. After adsorption NH<sub>3</sub> 30min, the catalyst was pretreated under helium flow 100 °C for 1 h to remove the adsorbed NH<sub>3</sub> from sample surface. Desorption curve was recorded from 100 °C to 800 °C at 10 °C /min.

X-ray photoelectron spectroscopy (XPS) analysis was conducted using an ESCALAB 250 Xi (Thermo, USA) X-ray photoelectron spectrometer with Al K $\alpha$  line as the excitation source (hv = 1484.6 eV) and adventitious carbon (284.6 eV for binding energy) was used as reference to correct the binding energy of sample.

TG analysis was performed with a STA409 instrument in dry air at a heating rate of 20 °C/min.

#### 2.4 Catalytic reaction

The carbonation reaction was carried out in a 100mL threenecked flask provided with magnetic stirrer. 25 mmol glycerol, 37.5 mmol urea and a certain amount of prepared catalysts (5 wt. % to glycerol) were added into flask. Carbonation reaction was performed at 140 °C for 6h under stirring, under reduced pressure of under 1kPa. After reaction completion, the mixtures were cooled to ambient temperature. Added 15 ml of methanol washed the catalyst. Subsequently, the reaction mixtures were separated from the catalyst by centrifugation and dried 12 hours. The supernatant was used for gas chromatography analysis. The washed catalyst was used in the next circulation.

#### 2.5 Product analysis

The supernatant was analyzed by gas chromatography 9790II. A quantitative analysis method of glycerol and glycerol carbonate by SE-54 capillary column gas chromatography with FID detector and using tetraglycol as internal standard was applied <sup>33-36</sup>. The injection volume of sample is 0.2  $\mu$ L. Temperature programming which increased from 60 °C to 260 °C and using of silyl reagent were adopted in the analysis. Silyl agent<sup>37-38</sup> was composed of the 4 mL DMF, 4 mL dioxane amine hexamethyldisilazane and 0.1 mL trimethylchlorosilane. Pipette 100  $\mu$ L of sample, followed by adding silyl reagent in tube. Subsequently, the tube was vibrated for 1 min and allowed to stand. The supernatant was analyzed by gas chromatography.

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#### 3. Results and discussion

#### 3.1 Characterization of catalysts

#### 3.1.1. FT-IR analysis

Before the detailed results with the three solid catalysts are presented, the activity of several heterogeneous catalysts were compared. The yield to glycerol carbonate was <100%, mainly due to the formation of byproduct. From the test results. ZnO from ZMG had the better catalytic activity due to porous structure. The results were displayed in Fig. 1. The FTIR spectra of ZnO, ZMG and ZnO from ZMG catalysts were showed in Fig.1. Zn glycerolate platelets were obtained via the glycerol-mediated synthesis utilizing a solution of Zn(CH<sub>3</sub>COO)<sub>2</sub> in glycerol that was heated to 150 °C. At about 120 °C the solution became turbid which indicates the precipitation of solid Zn glycerolate. Infrared spectra (FT-IR) of the as-prepared ZMG with platelike structure was also in complete agreement with reference data of Zn glycerolate. The narrowing of the glycerol bands in Zn glycerolate was due to the crystalline nature of the material. The characteristic signals of the alcoholic C-O stretching mode were present at 1054 and 1124 cm<sup>-1</sup>. The peaks at 1468 and 1675 cm<sup>-1</sup> were attributed to the O-H bending mode. The broad absorption peak at 3443 cm<sup>-1</sup> was attributed to the -OH group, such as water molecules in catalyst interlayer region, glycerol O-H stretching mode and hydrogen bonding. The band at 1943 cm<sup>-1</sup> assigned to C-O stretching mode, where the oxygen atom is involved in hydrogen bond, proves the existence of zinc glycerolate phase. The characteristic signals of the Zn-O in zinc glycerolate were present at 650.89 cm<sup>-1</sup> in Fig. 2(a), indicated the presence of Zn-O bond in the sample. The peak of ZnO from ZMG was consistent with ZnO. In fact, ZnO from ZMG and ZnO had characteristic signals in 650.89 cm<sup>-1</sup>. The surface of ZnO sample had bending and stretching vibration peak of hydroxyl group at 1632.78  $cm^{-1}$  and 1115.46  $cm^{-1}$  in Fig. 2(b) and Fig. 2(c). In the air, the sample surface adsorbed water, resulting in the formation of the hydroxyl peak.

#### 3.1.2 XRD analysis

The three different solid base catalysts about XRD patterns was shown in Fig. 3. The XRD profile of the synthesized ZMG with typical of layered compounds showed an intense basal diffraction attributed to the first basal peak in the region of 11° at 20 values. From Fig. 3(b), compared with standard card, the prominent crystalline phase ZMG catalysts are attributed to Zn



Fig. 1. Comparison of reusability of three catalysts (Reaction conditions: glycerol/urea=1:1.5, catalyst dosage 5.0 wt.%, 140 °C, 6 h, 1KPa)





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#### 3.1.3 SEM analysis

was inferior to ZnO obtained from ZMG.

The morphology of precursor ZMG before and after calcination by scanning electron microscopy, a representative picture were listed in Fig. 4. Surface morphologies of the ZMG samples were recorded using field emission scanning electron microscopy (FE-SEM) analysis, and the images were shown Fig. 4(a-b). It can be clearly seen that a large number of plate-like microcrystals of zinc glycerolate were formed. In addition, according to SEM images the morphology of ZMG were platelike, irregular and polygon. From the figure we can see, after calcination the sample had the porous layer structure Fig. 4(c-





Fig. 4. SEM of three solid catalysts (a-b): ZMG; (c-d): ZnO from ZMG; (e-f): ZnO

d). We speculate that the major change in morphology of the sample can be explained due to the loss of organic ligands results in phase transition from ZMG to ZnO at high temperature which was consistent with the XRD analysis as described earlier<sup>39</sup>. At the same time, the micrographs reveal that most of them are porous, irregularly shaped. The precursor ZMG after calcination transformed into ZnO. ZMG with plate-like morphology, its layered structure resulted in poor catalytic performance due to the non-porous in plate. Precursor ZMG after calcination had the porous layer structure contributed to the excellent catalytic performance. Comparison showed that, the morphology of ZnO displayed that sample were stacked together lead to nonporous and poor catalytic performance in Fig. 4(c-d).

#### 3.1.4. BET analysis

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Three different catalysts were analyzed by BET in Table 1. The specific surface area and pore size was described by the N<sub>2</sub> adsorption isotherm. Structural features improved significantly due to calcination, which may be attributed to improved crystalline phase of catalyst. Based on pore size, catalyst is divided into microporous, mesoporous and macroporous. Moreover, the high absorption at low relative pressure represents the microporous nature of materials. Among the three catalysts, the ZnO from ZMG catalyst possess the largest pore diameter and specific surface area. As seen from BET, the pore size of ZnO from ZMG catalyst was 48.156nm which matched with the characteristics of mesoporous materials, suggested that the catalyst was composed of mesoporous structures. It was observed that the surface area of ZMG was less than ZnO from ZMG, which could be attributed to the porous structure. The specific surface area and pore volume of ZnO obtained from Zn(OH)<sub>2</sub> was poor in Table.1. Mesoporous materials with relatively large specific surface area, pore size and regular pore structure can handle larger molecules or groups and improve the diffusion rate of the reactants. BET results are consistent with the results of SEM. The porous structure of catalyst which makes the catalyst a promising candidate for the industrial production of glycerol carbonate.

#### 3.1.5. Acid and base properties of catalysts

CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD was adopted to measure the basicity and the acidity of the catalysts. Largely, the catalytic performance of catalyst was affected by basicity and acidity of catalyst in Fig. 5(a) and Fig. 5(b). The CO<sub>2</sub> desorption capacity is proportional to the amount of base and the CO<sub>2</sub> desorption temperature represents the strength of basic sites. The CO<sub>2</sub> desorption curve was shown in Fig. 5(a). The ZnO catalyst exhibited a broad desorption peak in 400 °C. These desorption peaks are related to the weak basic sites in the catalyst. Whereas the ZnO from ZMG catalyst also presented a broad desorption peak in 400 °C. The integral area of the ZnO from ZMG catalyst was 4041.614. While, the integral area of the ZnO catalyst was 2916.536. Thus, from the integral area, the ZnO from ZMG catalyst had a high peak area which showed a stronger basicity.

The NH<sub>3</sub> desorption capacity is proportional to the amount of acid and the NH<sub>3</sub> desorption temperature represents the strength of acid sites. For acidity, the NH<sub>3</sub> desorption curve was shown in Fig. 5(b). The ZnO catalyst exhibited a broad desorption peak in the range of 250-350 °C. These desorption peaks are related to the weak acid sites in the catalyst. Whereas the ZnO from ZMG catalyst also presented two broad desorption peak respectively in 200-500 °C and 550-800 °C. These desorption peaks in 200-500 °C are related to the weak acid sites in the catalyst and desorption peaks in 550-800 °C are related to the strong acid sites in the catalyst. The NH<sub>3</sub> desorption integral area of the ZnO from ZMG catalyst was 5413.714. While, the NH<sub>3</sub> desorption integral area of the ZnO catalyst was 3132.736. Thus, from the integral area, the ZnO from ZMG catalyst had a high peak area which showed a stronger acidity. It can been seen from integral area that the acid property was nearly close to base property for ZnO from ZMG. In the carbonylation reaction, lewis acid catalyst activated urea carbonyl group, hydroxyl group of glycerol was activated conjugated basic sites. The results showed that with adequate combination of a weak Lewis acid and a Lewis base plays an important role in the high yield of glycerol carbonate. The base amount and acid amount of 7nO was inferior to 7nO

	Catalyst	BET surface area (m²/g)	pore volume (cm <sup>3</sup> /g)	pore diameter (nm)
-	ZnO from ZMG	13.71	0.04531	48.15
	ZMG	3.698	0.03752	16.15
	ZnO	1.178	0.004923	7.568

Tab.

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Fig. 5(a). TPD of  $CO_2$  profiles of two catalysts: ZnO and ZnO from ZMG solid catalysts



Fig. 5(b). TPD of  $\mathsf{NH}_3$  profiles of two catalysts: ZnO and ZnO from ZMG solid catalysts

#### from ZMG.

#### 3.1.6. XPS analysis

To gain more information about the ZnO nanoparticle, XPS was performed<sup>44</sup>. Fig. 6(a) exhibited the XPS survey spectrum of ZnO nanoparticle. The Fig. 6(a) indicated that XPS consist of Zn, O and trace amount of carbon in the results was mainly attributed to adventitious hydrocarbon from XPS itself. Fig 6(b) showed that the peaks of the Zn2p were found to be at 1021.68 eV and 1044.3 eV for Zn2p1/2 and Zn2p3/2, respectively<sup>45</sup>. We obtained binding energy of ZnO in the experiment were consistent with previously reported in the literature about Zn2p for ZnO. No obvious shift of the Zn2p peaks is observed and peak positions are closely matching with the standard value for ZnO, indicating that Zn atoms are in the 2+ oxidation state<sup>46</sup>. In Fig. 6(c), the peak of O1s were located at about 530.45 eV. The peak at 530.45 eV could be attributed to the bond formation between O and Zn. Namely, the peak at 530.45 eV was attributed to  $O^{2-}$  ions in  $ZnO^{47}$ .

#### 3.1.7. TG-MS

Thermal decomposition of Zn glycerolate had only a significant weight loss stage which correspond to the decomposition of



Fig. 6. XPS of ZnO from ZMG solid catalysts

organic compounds, weight loss rate of 37.28% in Fig. 7. From DTG curves of Zn glycerolate, there existed maximum weight loss of Zn glycerolate at 412 °C. Namely, at this temperature the decomposition of Zn glycerolate was fastest. This value matched exactly when assuming a thermal decomposition of Zn glycerolate in air under formation of ZnO. As can be seen from TG analysis and a temperature of 450 °C required for complete decomposition. Meanwhile, to prepare the catalyst with excellent hole-shaped morphology we need to control the calcination rate. High temperature and the high calcination rate will lead to the catalyst sintering. Therefore, Zn glycerolate was calcined at 450 °C with calcination rate at 0.5 °C/min.

#### 3.2. Catalytic activity

#### 3.2.1. Effect of reaction temperature

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Reaction temperature as one of the most important factors was investigated which could largely affect the carbonation reaction. The catalytic activities of the ZnO catalysts were studied with the reaction temperatures varying from 120 to 160  $^{\circ}$ C. The yield of glycerol carbonate were shown in Fig. S1 in supporting information. Increasing reaction temperature would improve catalytic reactivity. The results showed that the yields of glycerol carbonate firstly increased with the increase of reaction temperature and then decreased with further heating with a turning point 140  $^{\circ}$ C. In summary, the optimum reaction temperature is 140  $^{\circ}$ C. Chemical equilibrium constant calculations show the high temperature and low pressure is appropriate to synthesis glycerol carbonate by glycerol and urea.

#### 3.2.2. Effect of urea-to-glycerol molar ratio

It is well known that the carbonation reaction is an equilibrium reaction and that the excess amount of glycerol can drive the equilibrium toward product formation. In this reaction, glycerol reacted with urea in molar ratio 1:1.5 at 140 °C in the presence of a catalyst and usually under vacuum to shift the thermodynamic equilibrium by removing continuously the ammonia formed. Carbonation reaction was performed by varying the urea to glycerol molar ratios from 1:1 to 3:1 and at 140 °C till the completion of reaction (See Fig. S2 in supporting information). In the first stage, the yields of glycerol carbonate gradually increased until the maximum values. Further increase in the molar ratio of urea-to-glycerol beyond its optimum value would decrease the yield of glycerol carbonate. Hence, 1.5:1 molar ratio of urea to glycerol was selected for optimizing urea-to-glycerol molar ratio parameters.

#### 3.2.3. Effect of reaction time and dosage of catalyst

The reaction time was known to be one of the important parameters which could affect the fame yield. In my experiment, the glycerol carbonate yields of the reaction time varying from 3 to 7 h were investigated. As shown in Fig. S3 in supporting information, the maximum yield of glycerol was obtained at 6 h. As depicted, the formation of GC proceeds in two consecutive steps. The carbamate formed in the first step of the reaction and the glycerol carbonate was end-product<sup>48</sup>. With further increase of the reaction time, the generated glycerol carbonate would decompose into glycidol. Hence, the optimal reaction time for glycerol carbonate production was 6 h. The catalyst amount varied between 0.023-0.253 g (1–11)

wt.% with respect to glycerol amount), whereas the other reaction conditions were fixed, the molar ratio glycerol/urea of 1:1.5, reaction temperature of 140  $^{\circ}$ C, 1KPa and reaction time of 6h in Fig. S4. According to Fig. S4, it is clear that the addition of catalyst ameliorated the yield of GC.

#### 3.3 Catalyst stability tests

The stability of the catalyst ZnO from ZMG with porous, irregularly shaped was examined by testing the reusability of catalyst. The recyclability of catalyst is very important for industrial and technological applications. The catalyst recycling is an important step as it minimizes the cost of the process. The ZnO catalyst in each reaction separated by separator, washed with methanol and dried fully before reutilization. The stability of catalyst was investigated, as shown in Fig. 8. The glycerol carbonate yield could remain 70.85% after the catalyst was repeatedly used for five times. Recycling experiments was executed by employing it in the consecutive reaction for 6 times under the same conditions. After each reaction, the catalyst was fully washed with methanol over again and dried in oven overnight. In order to further explore the superiority of the ZnO catalyst on the catalytic performance, a comparison of ZnO, pure ZnO and ZMG had been made in repeatability. The retained performance illustrated that the activity of catalyst still exist after the circulation. The catalyst still showed excellent catalytic performance without significantly weaking. The particle size of porous ZnO catalyst maintained between 220nm to 235nm. The polydispersibility of porous ZnO catalyst was less than ZnO which demonstrated the excellent dispersion performance of catalyst (seen from Fig. S5). As acknowledged by XRD characterization aforementioned, the structure of the catalyst was essentially maintained during the recycling tests, and it was helpful with the good recycling performance. Therefore, porous ZnO catalyst with high activity, highly recyclable, remarkably stable, and environmental friendly is appropriately applied in industrialization.

#### 4. Conclusions

In short, the heterogeneous catalysts by prepared can be applied for synthesis glycerol carbonate in industrial



Fig. 8. Comparison of reusability of three catalysts (Reaction conditions: glycerol/urea=1:1.5, catalyst dosage 5.0 wt.%, 140  $^{\circ}$ C, 6 h, 1KPa)

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production. Compared with different catalysts, the maximum glycerol carbonate yield 85.97% with the ZnO from ZMG as the catalyst under optimizing operating conditions was obtained. Reaction test indicated that the catalysts with appropriate acid and base properties were favorable to the synthesis of glycerol carbonate. The catalyst still has excellent catalytic performance after 5 cycles, almost no loss of catalytic activity. The study revealed that the ZnO catalyst having the advantages of high activity, highly recyclable, remarkably stable, and environmental friendly is appropriately applied in industrialization. A green cogeneration of high purity of zinc glycerolate( ZMG) and glycerol carbonate( GC) was established by using glycerol as the main raw material. In this study, glycerol can be relevant for applications such as reactants and as raw material to prepare the catalyst. Furthermore, the reaction product of ammonia can also be used in the next reaction to synthesize urea. We hope that our work can make contribution to the industrialization of glycerol carbonate.

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