

Research Article

Synthesis of Glycerol Carbonate from Glycerol and Dimethyl Carbonate Catalyzed by Solid Base Catalyst Derived from Waste Carbide Slag

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Na_2CO_3 was loaded onto waste carbide slag (CS) by impregnation-calcination method to prepare the solid base catalyst, which was used to synthesize glycerol carbonate (GC) by the transesterification of glycerol with dimethyl carbonate (DMC). The prepared catalysts were characterized by a scanning electron microscope (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Brunner–Emmet–Teller (BET) techniques. The catalyst 15 wt.% Na_2CO_3 -CS-800, which was prepared by impregnating CS to the Na_2CO_3 solution with the concentration of 15 wt.% weight of CS and calcined at 800°C for 3 hours, showed an excellent catalytic ability. When it was applied in the catalytic synthesis of GC, 98.1% glycerol conversion and 96.0% GC yield were achieved in 90 mins at 75°C with the catalyst dosage of 3 wt.% to total reactants and the DMC to glycerol molar ratio of 5. More importantly, the loading of Na_2CO_3 can effectively improve the reusability of catalyst. The 15 wt.% Na_2CO_3 -CS-800 can still achieve 83.6% glycerol conversion and 80.5% GC yield after five-time reuse. Meanwhile, under the same reaction conditions, the CS-800, which was obtained by calcining CS at 800°C for 3 hours, experienced significant activity reduction with only 15.2% glycerol conversion and 14.1% GC yield after five-time reuse. FTIR and XRD characterization revealed that CO_3^{2-} might play a key role in preserving active catalytic CaO component by forming protective CaCO_3 shell on the catalyst surface.

1. Introduction

The demand of human society for energy is increasing, but the nonrenewable fossil fuels on the earth are decreasing. Therefore, it is more and more important to seek green and sustainable energy as an alternative to traditional fossil fuels [1, 2]. As a new environmentally friendly biomass fuel, biodiesel has been developed rapidly in recent decades because of its good performance of nontoxic, low pollution, and biodegradability [3–5]. However, the industrial production of biodiesel has to face the problem of disposal of by-product, glycerol. In general, 1 kg of glycerol will be produced for every 10 kg of biodiesel production [6, 7]. The pro-

duced glycerol is dumped as industrial waste, which can cause serious economic loss and environmental pollution [8]. Therefore, the high value-added utilization of glycerol has aroused the interest of researchers and becomes a research hotspot [9].

GC is one of the high value-added glycerol derivatives because of its excellent properties such as biodegradability, low flammability, nontoxicity, and high boiling point [10, 11]. It is widely used not only in the manufacture of polymer products, like gas separation membranes, coatings, and inks [12, 13] but also as an important synthon for functional polymer preparation [14–16]. The methods that utilize glycerol as feedstock for synthesizing GC mainly include (i) the

reaction of glycerol with phosgene [17, 18], (ii) the oxidation carbonylation of CO [19, 20], (iii) the reaction of glycerol with CO₂ [21, 22], (iv) the glycerolysis of urea [23, 24], and (v) the transesterification of glycerol with dimethyl carbonate [25, 26]. Among these methods, methods (i) to (iv) have obvious drawbacks, which hindered their widespread applications for the synthesis of GC. In methods (i) and (ii), highly toxic reactants were used, and there are potential safety hazards in the synthesis process. In method (iii), the reaction of glycerol with carbon dioxide is green and environmentally friendly. However, the reaction condition is extremely harsh and the yield of GC is not desirable. The glycerolysis of urea needs purge gas or vacuum decompression to remove by-product NH₃. In contrast, the transesterification of glycerol with DMC is an environmentally friendly method and can be carried out under mild reaction conditions [27]. Therefore, this method has become a common method for GC synthesis.

Catalyst plays an important role in the transesterification of glycerol with DMC. Several factors, such as catalytic performance, separation efficiency, and environmental friendliness, should be considered in the selection of catalyst. Usually, the transesterification reaction between glycerol and DMC is catalyzed by base catalysts, which include homogeneous catalysts and heterogeneous catalysts. Homogeneous base catalysts such as KOH and triethylamine show high catalytic performance [28]. However, it is difficult to separate catalyst from product mixture. The presence of homogeneous base catalyst in the reaction intermediate reduces the purity of the final product [29]. In contrast, heterogeneous base catalysts exhibit greater advantages in both separation efficiency and environmental friendliness. Therefore, more and more attention has been paid to the research of heterogeneous base catalysts. However, heterogeneous base catalysts also show some drawbacks in the transesterification reaction of glycerol with DMC. For example, metal oxide catalysts such as CaO [30] and Mg_{1+x}Ca_{1-x}O₂ [31] are easily polluted by H₂O and CO₂ in the environment, metal salt catalysts such as NaAlO₂ [32] can leach active sites in the reaction process, and supported catalysts such as NaOH/ γ -Al₂O₃ are time-consuming in its preparation [33]. In addition to catalytic performance, separation efficiency, and environmental friendliness, the cost of the catalyst preparation is also a key factor that should be considered. Ionic liquids [34, 35] and biological enzymes [36, 37] as new green catalysts have attracted great attention. However, the complex preparation process and relatively high preparation cost seriously limit the application of these catalysts in the industrial field. Therefore, it is an urgent task to develop heterogeneous base catalysts with high activity and low cost.

In recent years, using natural minerals and wastes to develop new materials has become a new trend. [38] Since using waste to prepare material has the advantage of low cost, heterogeneous base catalysts derived from waste have attracted extensive attention in the field of GC synthesis [39]. These catalysts exhibit an outstanding catalytic performance in the synthesis of GC and could be easily recycled and reused. The waste materials that are used to prepare cat-

alyst mainly include the municipal waste, industrial waste, biomass waste, and agricultural waste, such as baby diapers [40], red mud [41], steel slag [42], coal fly ash [43], oil palm fuel ash [44], crayfish shell [45], and corncob [46].

CS is an alkaline solid waste that is generated in the production of ethyne. The composition of CS includes Ca(OH)₂, CaCO₃, and small amounts of MgO, SiO₂, Al₂O₃, Fe₂O₃ [47]. The annual output of CS is about 5.6×10^7 tons in China [48]. CS can be used as raw material to prepare cement binder or acid gas absorbent. However, only 40% of CS could be recycled, while the remaining 60% would be disposed as solid hazardous waste [49]. The stacked CS waste has occupied a large amount of land and must be buried or covered in order to prevent air pollution in windy weather. However, the burial of CS would inevitably cause serious damage to soil and groundwater. Therefore, large-scale recovery and reuse of CS are of great significance. However, in the synthesis of GC, it is well recognized that the Ca-based catalyst suffers from serious stability issues, such as readily absorption of CO₂ and H₂O from the air as well as leaching into reaction mixtures [44].

In this work, to turn abundant hazardous waste CS into valuable catalyst and, more importantly, to improve the stability of Ca-based alkaline catalyst, Na₂CO₃ was introduced into CS by impregnation-calcination method. The surface morphology, chemical composition, and total basicity of the resultant catalysts were characterized by SEM, TGA, FTIR, XRD, BET, and acid-base titration techniques. Afterwards, catalysts were applied in the transesterification of glycerol with DMC. The effect of reaction conditions on glycerol conversion and GC yield was studied. Finally, the catalytic mechanism of the catalyst was proposed.

2. Materials and Methods

2.1. Materials. CS was purchased from a sewage treatment plant in China. Analytical grade glycerol was obtained from Macklin, China. Analytical grade pyridine, ethanol, sodium carbonate, and DMC were purchased from Aladdin, China. The abovementioned chemicals were directly used without further purification.

2.2. Catalyst Preparation. First, CS was screened with 100-mesh standard sieve to remove large particles and impurities and then dried for 2 hours at 100°C. 5 g of dried CS was impregnated in 5 ml solution with different Na₂CO₃ contents (0%, 5%, 10%, 15%, and 20% weight of CS) and then stirred for 15 mins and stood for 24 hours at room temperature. After that, the impregnated sample was heated for 3 hours at 100°C to remove moisture. Finally, a series of solid base catalysts were prepared by calcining samples in a muffle furnace at 500°C, 600°C, 700°C, 800°C, and 900°C for 3 hours. The prepared catalyst was named as $n\text{Na}_2\text{CO}_3\text{-CS-}T$, where n represents the weight percentage of Na₂CO₃ to CS and T represents the calcination temperature. For example, when the loading of Na₂CO₃ was 5 wt.% of CS and calcination temperature was 800°C, the obtained catalyst was named as 5 wt.% Na₂CO₃-CS-800. When the loading of Na₂CO₃ was 0 wt.%, the prepared catalyst was abbreviated

as CS-T. The amount of the raw materials used in the catalyst preparation is shown in Table 1.

2.3. Catalyst Characterization. The surface morphology of CS-derived catalyst was observed by SEM (S-3700N, Japan). TGA and derivation thermogram (DTG) were obtained from a Mettler TGA/DSC3+ equipment (35°C~900°C, 20°C/min, air atmosphere). FTIR (Nicolet iS50) was used to characterize the functional groups of catalysts (4000 cm⁻¹~400 cm⁻¹). The crystallization of CS-derived catalysts was characterized by XRD (Rigaku Ultima IV). The test conditions are as follows: CuK α radiation ($\lambda = 0.1540$ nm), 40 kV, 30 mA, scanning rate 10°/min, and scanning range $2\theta = 3 - 90^\circ$. The pore volume, pore diameter, and BET surface area of CS-derived catalysts were measured by the nitrogen adsorption/desorption isotherms using a JW-BK122W instrument (JWGB, China). Moreover, the total basicity of CS-derived catalyst was obtained by the acid-base titration technique.

2.4. Transesterification Reaction. The transesterification reaction between glycerol and DMC was carried out in a 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser. In a typical reaction, glycerol (2.76 g, 0.03 mol) and DMC (13.51 g, 0.15 mol) were added into the flask, and then, the reactants are heated in an oil bath. When the temperature reached 75°C, the catalyst that weighed 3% of total reactants was added and stirred for 90 mins. Afterwards, the catalyst was separated by simple filtration, and the obtained liquid crude product was weighed. An internal standard method that used tetraethylene glycol as internal standard sub-

TABLE 1: The amount of the raw materials in the catalyst preparation.

Catalyst	CS (g)	Na ₂ CO ₃ (g)	Na ₂ CO ₃ loading (wt.%)	H ₂ O (ml)
CS-T	5	0	0	0
5 wt.% Na ₂ CO ₃ -CS-T	5	0.25	5	5
10 wt.% Na ₂ CO ₃ -CS-T	5	0.50	10	5
15 wt.% Na ₂ CO ₃ -CS-T	5	0.75	15	5
20 wt.% Na ₂ CO ₃ -CS-T	5	1.00	20	5

T was calcination temperature, including 500°C, 600°C, 700°C, 800°C, and 900°C.

stance was adopted to quantitatively analyze the product of transesterification reaction by gas chromatography (Agilent Technologies, 7820A) [45]. Gas chromatograph was equipped with a flame ionization detector using a DB-5 capillary column (Agilent Technologies, 60 m \times 0.320 mm). The heating procedure of gas chromatography column was as follows: keeping at 60°C for 10 min firstly, then heating up to 260°C at the speed of 20°C/min, and keeping at 260°C for 6 min finally. Glycerol conversion and GC yield were used as the main parameters to investigate the catalytic ability of the catalyst [50]. The glycerol conversion and GC yield were calculated the same as reported by literature [51].

$$\text{Glycerol conversion} = \frac{\text{Initial mole number of glycerol} - \text{residual mole number of glycerol}}{\text{Initial mole amount of glycerol}} \times 100\%,$$

$$\text{GC yield} = \frac{\text{Mole number of GC}}{\text{Initial mole number of glycerol}} \times 100\%.$$
(1)

2.5. Catalyst Reusability Experiments. Reusability is an important property of solid base catalyst. Therefore, the reusability of optimal catalyst was investigated by recycling experiment under optimal reaction condition [40]. Firstly, the catalyst was separated from reaction mixture by filtration at the end of reaction. After that, the obtained catalyst was washed with ethanol to remove organic residues adhered to its surface. Finally, the washed catalyst was dried in an oven at 100°C for 1 h. The regenerated catalyst was reused for the transesterification. Finally, XRD and FTIR were adopted to analyze the reason for the decrease of catalytic activity.

3. Results and Discussion

3.1. Effect of Na₂CO₃ Loading and Calcination Temperature on Catalyst Activity. The effect of Na₂CO₃ on glycerol con-

version and GC yield was performed by using catalysts with different Na₂CO₃ loading. Taking the catalyst nNa₂CO₃-CS-800 as an example (Figure 1), when the DMC-to-glycerol molar ratio was 4:1, the reaction temperature was 75°C, reaction time was 120 mins, and catalyst dosage was 3 wt.%, glycerol conversion, and GC yield increased to the highest point with the increase of Na₂CO₃ loading from 0 wt.% to 15 wt.%. When CS-800 (0 wt.% Na₂CO₃) was used to catalyze the transesterification of glycerol with DMC, glycerol conversion and GC yield were 90.6% and 87.4%, respectively. When the loading amount of Na₂CO₃ reached 15 wt.%, glycerol conversion and GC yield increased by 4.4% and 4.6%, respectively. However, when the loading amount of Na₂CO₃ was further increased to 20 wt.%, glycerol conversion and GC yield did not change obviously. This result indicates that the optimum loading amount of Na₂CO₃ was 15 wt.%.

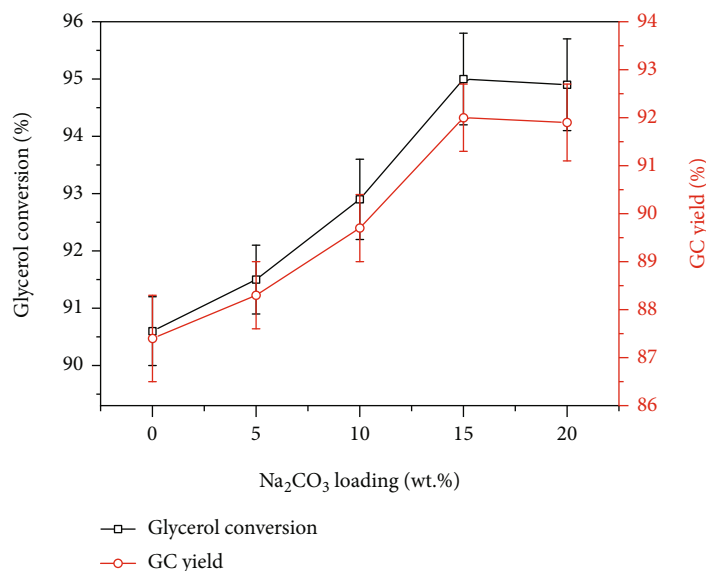
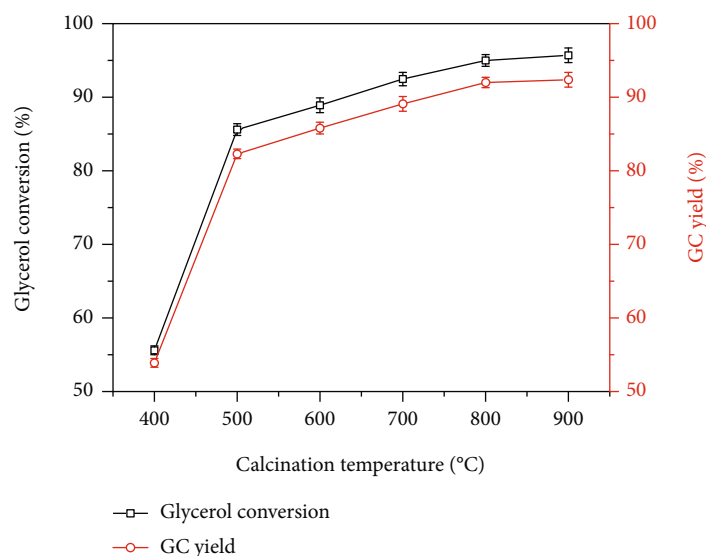
FIGURE 1: Effect of Na₂CO₃ loading on glycerol conversion and GC yield.

FIGURE 2: Effect of calcination temperature on glycerol conversion and GC yield.

Calcination temperature is also affecting catalytic activity [41]. Therefore, the effect of calcination temperature on glycerol conversion and GC yield was studied. Since the optimum loading of Na₂CO₃ had been determined, the following transesterification reaction was carried out with 15 wt.% Na₂CO₃-CS-T. Meanwhile, the DMC-to-glycerol molar ratio was 4:1, reaction temperature was 75°C, reaction time was 120 mins, and catalyst dosage was 3 wt.%. The results are shown in Figure 2. The catalyst corresponding to 100°C calcination temperature treatment was 15 wt.% Na₂CO₃-CS-100, which has the lowest catalytic activity with glycerol conversion and GC yield of 55.6% and 53.9%, respectively. When the calcination temperature was increased to 800°C, an obvious increase in catalytic activity was observed. Glycerol conversion increased from 55.6% to 95.0%; meanwhile, GC yield increased from 53.9% to

92.0%. This result shows that the increase of calcination temperature could effectively enhance the catalytic activity of the catalyst. The 15 wt.% Na₂CO₃-CS-800 and the 15 wt.% Na₂CO₃-CS-900 exhibited similarly high catalytic activity, which indicated the further increase of calcination temperature could not result in an obvious enhancement of glycerol conversion and GC yield. From the perspective of energy consumption, 800°C was the better calcination temperature. Thereafter, 15 wt.% Na₂CO₃-CS-800 was chosen as the most suitable catalyst for the transesterification of glycerol with DMC.

3.2. Catalyst Characterization. The surface morphology of the CS-800 and the 15 wt.% Na₂CO₃-CS-800 was observed by SEM, as shown in Figure 3. The CS-800 was composed of irregular lumps, and there are many interconnected holes

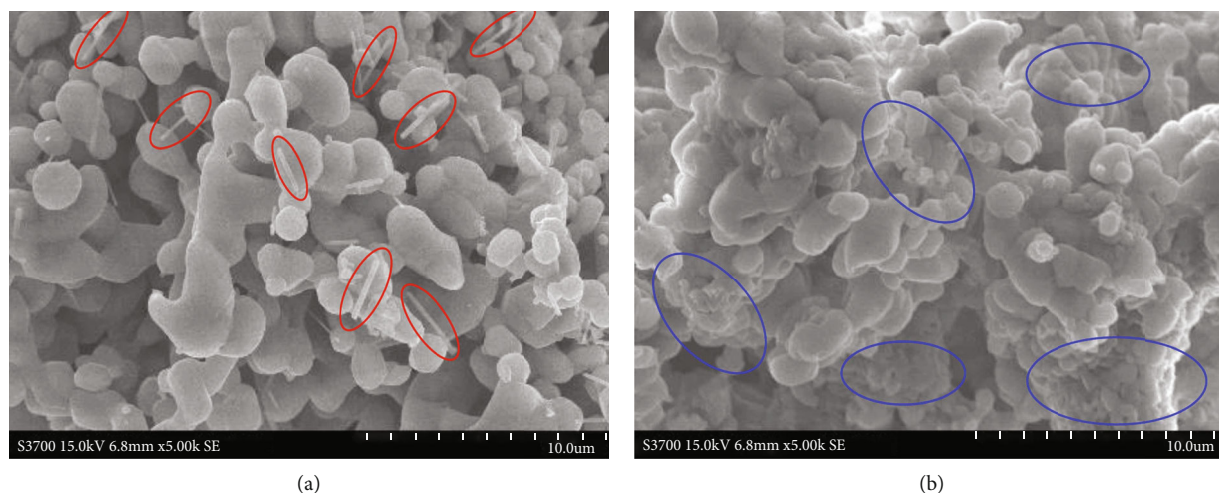


FIGURE 3: Morphology of (a) CS-800 and (b) 15 wt.% Na_2CO_3 -CS-800.

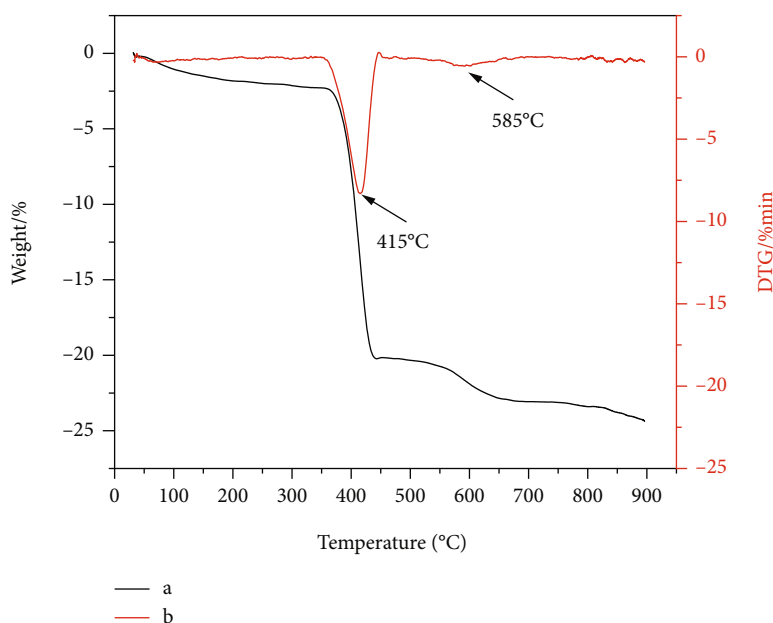


FIGURE 4: TGA and DTG curves of 15 wt.% Na_2CO_3 -CS-100.

and rod-shaped substances (red circle). Compared with CS-800, 15 wt.% Na_2CO_3 -CS-800 had a rougher surface structure, and numerous small granular bulges (blue circle) were observed on the surface. The rod-shaped substances also disappeared. The SEM images showed that the addition of Na_2CO_3 had changed the morphology of CS-800.

The thermal decomposition behavior of catalyst was characterized by TGA and DTG. As shown in Figure 4, the weight loss of 15 wt.% Na_2CO_3 -CS-100 during heating process can be divided into three stages. The first stage occurred at the temperature below 200°C. In this stage, a slight weight loss of approximately 2% was observed, which was ascribed to the evaporation of the physically absorbed moisture. The second stage took place in the temperature range of 350°C to 450°C, and the maximum weight loss temperature was 415°C. A rapid weight loss of approximately 18% was

observed, which was mainly assigned to the decomposition of $\text{Ca}(\text{OH})_2$ into CaO [52]. The third stage happened in the temperature range from 550°C to 650°C. A relatively slower weight loss of approximately 2% was noted. In this stage, the weight loss was attributed to the degradation of carbonate [53]. The TGA showed when the 15 wt.% Na_2CO_3 -CS-100 was calcined at different temperatures; the composition of its residue was different, leading to different catalytic activities.

As FTIR spectra can determine the main functional groups of the catalyst, the CS-800 and the 15 wt.% Na_2CO_3 -CS-800 were characterized by FTIR to investigate the effect of Na_2CO_3 loading on the functional groups of two catalysts (Figure 5). Both CS-800 and the 15 wt.% Na_2CO_3 -CS-800 showed a wide absorption peak around 3416 cm^{-1} , which was ascribed to the absorption of H_2O in

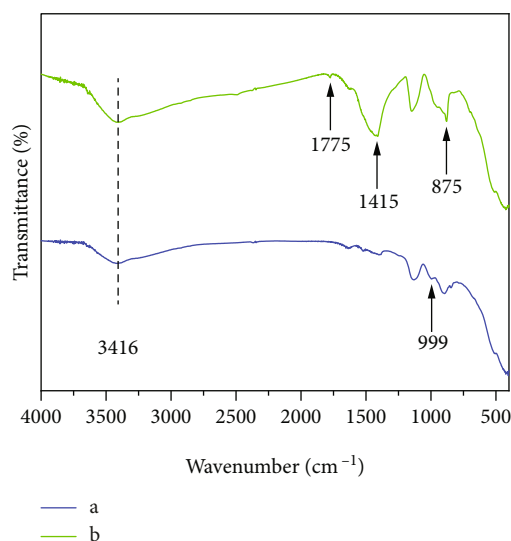


FIGURE 5: FTIR spectra of the (a) CS-800 and (b) 15 wt.% Na_2CO_3 -CS-800.

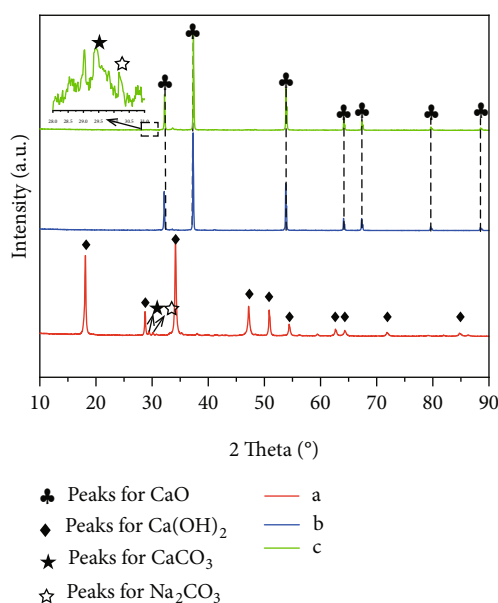


FIGURE 6: XRD patterns of the (a) 15 wt.% Na_2CO_3 -CS-100, (b) CS-800, and (c) 15 wt.% Na_2CO_3 -CS-800.

TABLE 2: Surface properties and total basicity of catalysts.

Catalyst	Pore volume (cm^3/g)	Pore diameter (nm)	BET surface area (m^2/g)	Total basicity (mmol/g)
CS-800	0.314	8.8	0.96	27.6
15 wt.% Na_2CO_3 -CS-800	0.269	7.3	0.82	32.1

the air. The peak at 999 cm^{-1} was assigned to the characteristic absorption peak of Si-O_2 , which indicated that CS contains a certain amount of SiO_2 [54]. The FTIR spectra of the 15 wt.% Na_2CO_3 -CS-800 showed three absorption peaks at 875 cm^{-1} , 1415 cm^{-1} , and 1775 cm^{-1} , which were the typical vibration peaks of CO_3^{2-} [40, 55]. The three peaks were not found in the FTIR spectra of the CS-800, which means CO_3^{2-} were mainly derived from Na_2CO_3 . That is to say, the added CO_3^{2-} was not decomposed completely during calcination process.

To further study the effect of Na_2CO_3 loading on the crystalline structure of the catalyst, XRD characterization on the 15 wt.% Na_2CO_3 -CS-100, CS-800, and 15 wt.% Na_2CO_3 -CS-800 was carried out. As shown in Figure 6(a), the prepared 15 wt.% Na_2CO_3 -CS-100 was mainly composed of Ca(OH)_2 . In addition, the diffraction peaks of Na_2CO_3 and CaCO_3 can be observed at 30.2° and 29.4° , respectively. It can be seen from Figure 6(b) that the CS-800 was mainly composed of CaO , which means that CS decomposed to CaO at 800°C . As to the 15 wt.% Na_2CO_3 -CS-800 (Figure 6(c)), despite the sharp diffraction peaks of CaO , the weak diffraction peak of Na_2CO_3 and CaCO_3 still can be observed at 30.2° and 29.4° , which demonstrated that 15 wt.% Na_2CO_3 -CS-800 was comprised of CaO , Na_2CO_3 , and CaCO_3 .

Table 2 presents the pore volume, pore diameter, BET surface area, and total basicity of the CS-800 as well as the 15 wt.% Na_2CO_3 -CS-800. It could be found that the pore volume, pore diameter, and BET surface area of 15 wt.% Na_2CO_3 -CS-800 were smaller than those of CS-800, which indicated the loading of Na_2CO_3 resulting in the decrease in pore volume, pore diameter, and BET surface area of the catalyst. The unreacted Na_2CO_3 and newly formed CaCO_3 had blocked or narrowed down the holes of the catalyst to a certain extent. Nevertheless, the loading of Na_2CO_3 increased the total basicity of the catalyst. The total basicity of 15 wt.% Na_2CO_3 -CS-800 was 4.5 mmol/g higher than that of CS-800. This result elucidated the basicity of the catalyst played an important role during transesterification.

3.3. Effect of Reaction Time on the Transesterification of Glycerol with DMC. Short reaction time will lead to incomplete reaction between glycerol and DMC, but long reaction time will produce more by-products [43]. Therefore, finding an optimized reaction time is very important for the transesterification of glycerol and DMC. Herein, the effect of reaction time on the transesterification of glycerol with DMC was studied. As shown in Figure 7, when the DMC-to-glycerol molar ratio was 5:1, reaction temperature was 75°C , and catalyst dosage was 3 wt.%, and glycerol conversion and GC yield increased significantly as the reaction time increased from 30 mins to 90 mins. When the reaction time was 30 mins, glycerol conversion and GC yield were 65.5% and 56.3%, respectively. When the reaction time reached 90 mins, glycerol conversion and GC yield were 94.6% and 91.4%, respectively. However, with the further increase of reaction time, glycerol conversion and GC yield did not change obviously. These results showed that the most suitable reaction time was 90 mins when 15 wt.% Na_2CO_3 -CS-

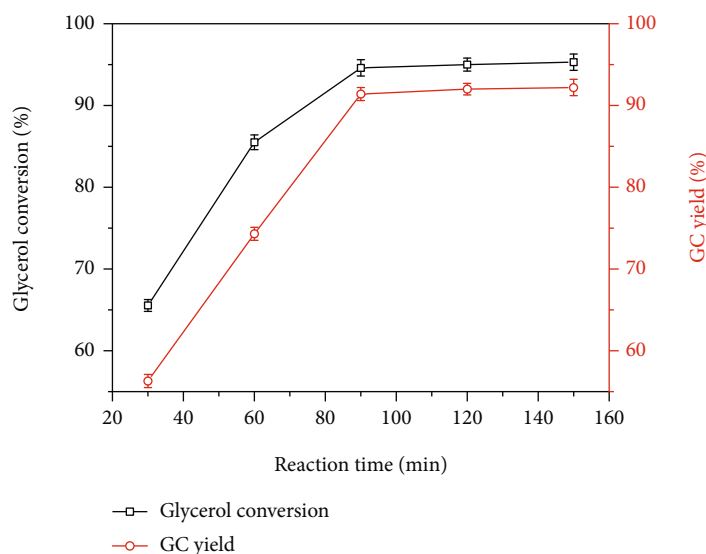


FIGURE 7: Effect of reaction time on glycerol conversion and GC yield.

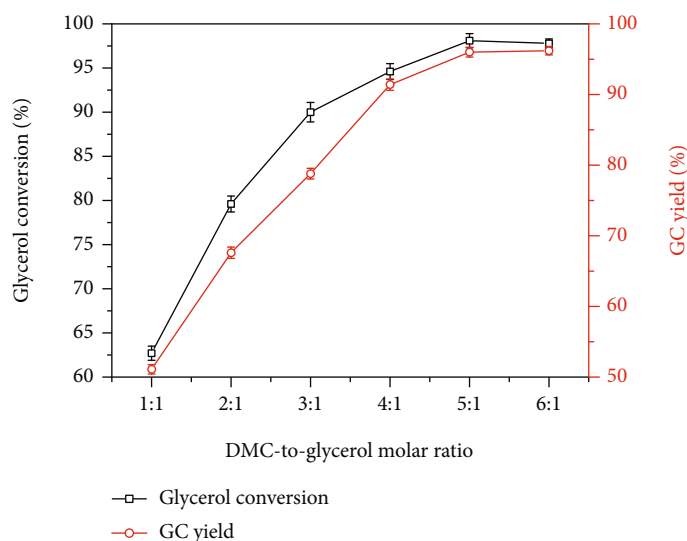


FIGURE 8: Effect of DMC-to-glycerol molar ratio on glycerol conversion and GC yield.

800 was used as catalyst for transesterification of glycerol with DMC.

3.4. Effect of DMC-to-Glycerol Molar Ratio on the Transesterification of Glycerol with DMC. Generally speaking, an appropriate increase in the amount of DMC usage can increase glycerol conversion rate, thereby increasing the GC yield. However, excessive DMC will limit the full contact between glycerol and catalyst [40]. Therefore, the effect of DMC-to-glycerol molar ratio on the transesterification of glycerol to DMC was studied. The reaction conditions were as follows: reaction time was 90 mins, reaction temperature was 75°C, and catalyst dosage was 3 wt.%. As shown in Figure 8, glycerol conversion and GC yield increased with the increase of DMC-to-glycerol mole ratio when the ratio was lower than 5:1. When the ratio was 5:1, glycerol conversion and GC yield reached 98.1% and

96.0%, respectively. However, when the DMC-to-glycerol molar ratio was higher than 5:1, there was no obvious change in glycerol conversion and GC yield. This result showed that the best mole ratio was 5:1 when the 15 wt.% Na_2CO_3 -CS-800 was used as catalyst to catalyze the transesterification reaction between glycerol and DMC.

3.5. Effect of Reaction Temperature on the Transesterification of Glycerol with DMC. The higher reaction temperature means the higher molecule thermal motion speed, leading to the higher reaction rate. Therefore, the effect of reaction temperature on the transesterification of glycerol with DMC was investigated under the conditions of reaction time 90 min, DMC-to-glycerol molar ratio 5:1, and catalyst dosage 3 wt.%. As shown in Figure 9, when the reaction temperature increased from 60°C to 75°C, glycerol conversion increased rapidly from 70.8% to 98.1% and the yield of GC

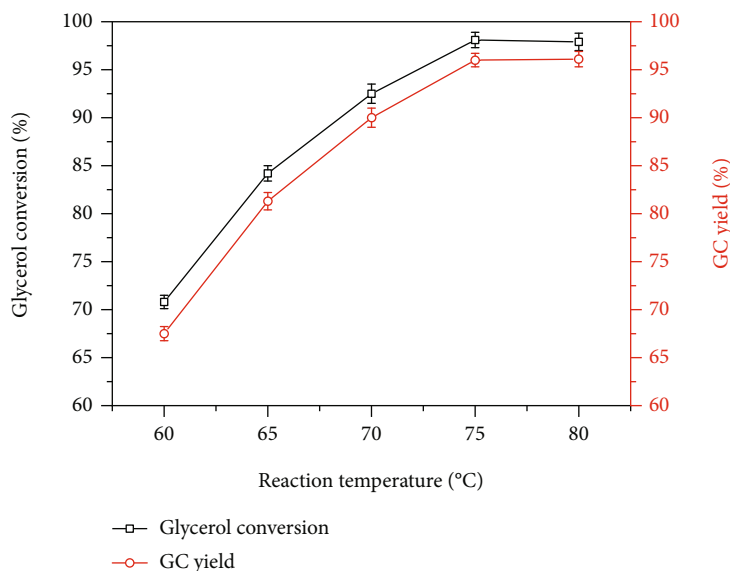


FIGURE 9: Effect of reaction temperature on glycerol conversion and GC yield.

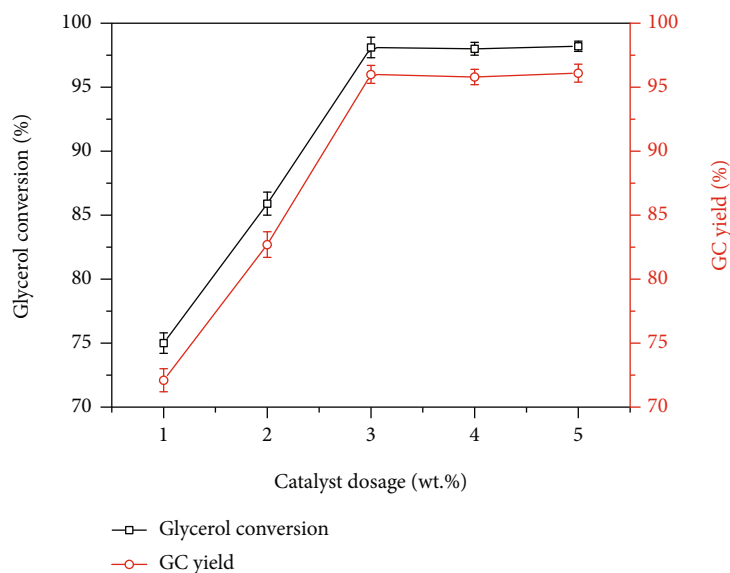


FIGURE 10: Effect of catalyst dosage on glycerol conversion and GC yield.

went up from 67.5% to 96.0%. However, when the reaction temperature was further increased, both glycerol conversion and GC yield were not improved obviously. This result showed that when 15 wt.% Na_2CO_3 -CS-800 was used as catalyst, the optimum reaction temperature for transesterification of glycerol with DMC was 75°C.

3.6. Effect of Catalyst Dosage on the Transesterification of Glycerol with DMC. The number of active sites in the reaction system depends on the amount of catalyst, and the reaction rate can be effectively increased by increasing the amount of catalyst properly. However, when the amount of catalyst exceeds a certain value, the aggregation and mass transfer resistance of catalyst particles will hinder the

improvement of glycerol conversion and GC yield [56]. Thus, it is important to find an appropriate catalyst dosage for the transesterification reaction between glycerol and DMC. Based on this, the effect of catalyst dosage on the transesterification of glycerol with DMC was studied. As shown in Figure 10, when reaction time was 90 mins, the DMC-to-glycerol molar ratio was 5:1, the reaction temperature was 75°C, and glycerol conversion and GC yield showed an increasing trend with catalyst dosage increased from 1 wt.% to 3 wt.%. When the catalyst dosage was 1 wt.%, glycerol conversion was only 75.0%, and GC yield was 72.1%. When catalyst dosage increased to 3 wt.%, glycerol conversion and GC yield increased to 98.1% and 96.0%, respectively. However, glycerol conversion and GC

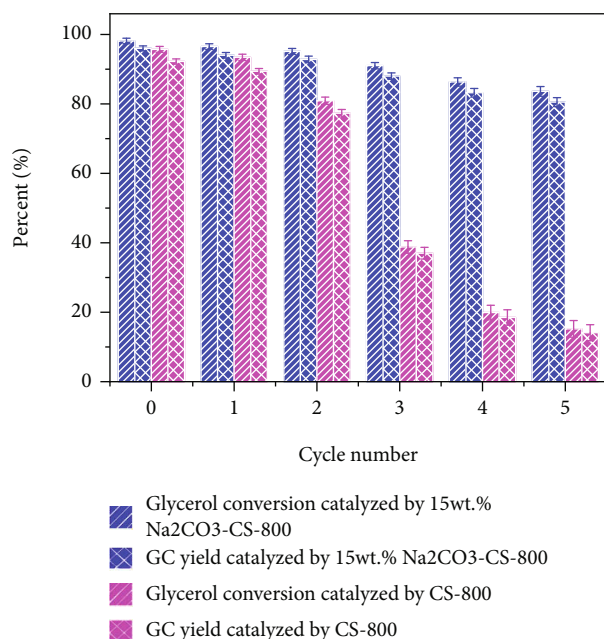


FIGURE 11: Reusability of the CS-800 and the 15 wt.% Na_2CO_3 -CS-800 in the transesterification of glycerol with DMC.

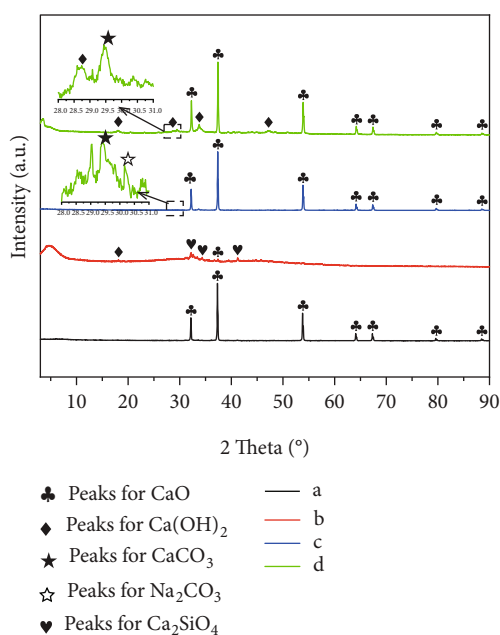


FIGURE 12: XRD patterns of (a) the CS-800, (b) the reused CS-800, (c) the 15 wt.% Na_2CO_3 -CS-800, and (d) the reused 15 wt.% Na_2CO_3 -CS-800.

yield did not change significantly with further increase of catalyst usage. This result showed that when 15 wt.% Na_2CO_3 -CS-800 was used as catalyst for transesterification of glycerol with DMC, the optimum catalyst dosage was 3 wt.%.

To sum up, optimized reaction conditions for transesterification of glycerol with DMC were determined as follows: reaction time 90 min, the DMC-to-glycerol molar ratio was

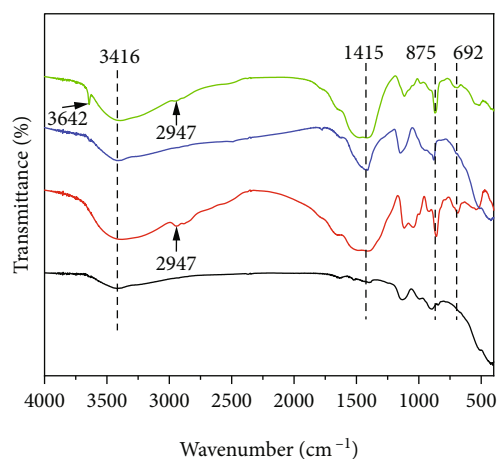


FIGURE 13: FTIR spectra of (a) the CS-800, (b) the reused CS-800, (c) the 15 wt.% Na_2CO_3 -CS-800, and (d) the reused 15 wt.% Na_2CO_3 -CS-800.

5 : 1, reaction temperature was 75°C , and 15 wt.% Na_2CO_3 -CS-800 dosage was 3 wt.%.

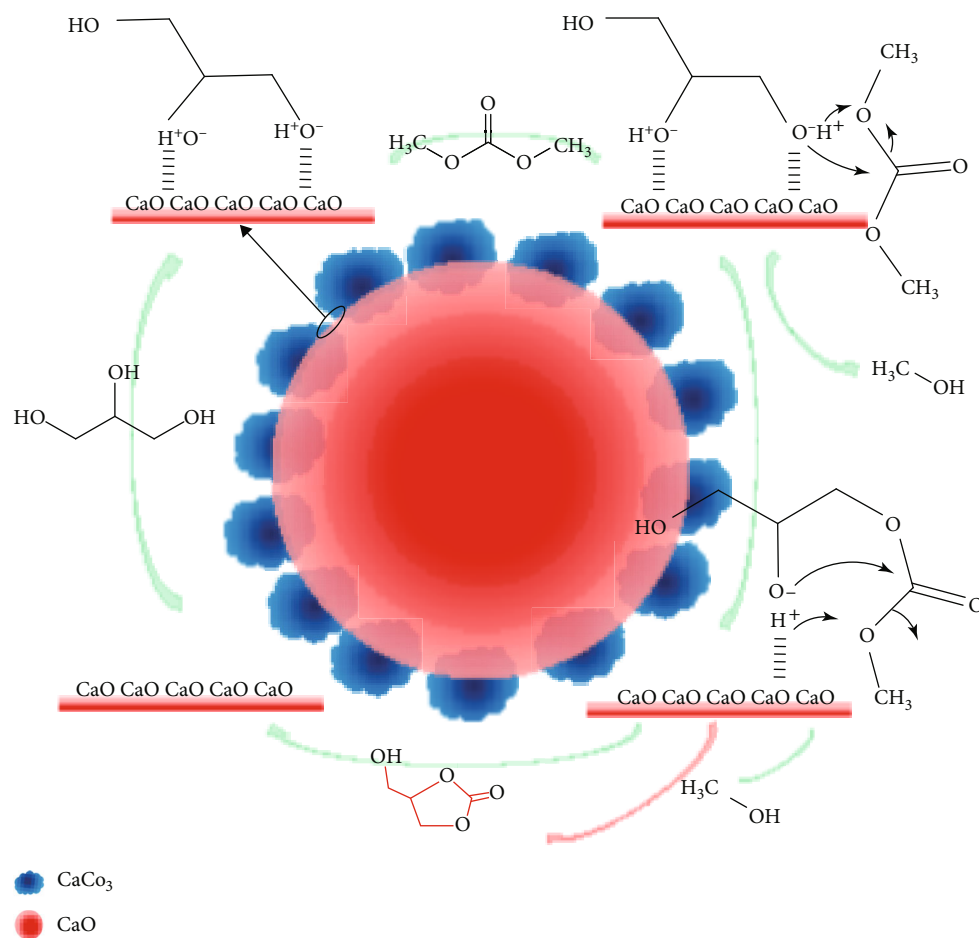
3.7. Catalyst Reusability. The solid base catalyst for industrial application must have a certain degree of reusability. The so-called reusability refers to a solid base catalyst that can be recycled for many times in reaction without obvious deactivation [57]. Therefore, recycling experiments based on CS-800 and 15 wt.% Na_2CO_3 -CS-800 were carried out under optimized reaction conditions. It can be seen in Figure 11 that when the transesterification of glycerol with DMC was carried out with 15 wt.% Na_2CO_3 -CS-800 as catalyst under the optimized reaction conditions, glycerol conversion and GC yield both showed a slow tendency to decrease. However, the conversion of glycerol was 83.6% and the yield of GC was 80.5% even after five cycles of the reaction. This result indicated that the 15 wt.% Na_2CO_3 -CS-800 exhibited a good reusability in the transesterification reaction of glycerol with DMC. In contrast, the reusability of CS-800 was much worse. When CS-800 was used to catalyze the transesterification reaction of glycerol with DMC for the first time, glycerol conversion was 95.7% and GC yield was 92.2%, respectively. However, after five cycles of the reaction, the conversion of glycerol was only 15.2% and the yield of GC was only 14.1%. Therefore, the CS-800 showed poor reusability. This striking contrast indicated that the loading of Na_2CO_3 can effectively improve the reusability of catalyst.

In order to clarify the deactivation mechanism of the CS-800 and the satisfactory reusability of 15 wt.% Na_2CO_3 -CS-800, XRD and FTIR were adopted to analyze the crystalline structure and composition of catalysts. Figure 12 shows the XRD patterns of the CS-800, the reused CS-800, the 15 wt.% Na_2CO_3 -CS-800, and the reused 15 wt.% Na_2CO_3 -CS-800. The XRD patterns of four catalysts showed three groups of characteristic diffraction peaks: (i) peaks at 18.0° , 28.9° , 33.9° , and 47.3° were attributed to the characteristic diffraction peak of $\text{Ca}(\text{OH})_2$ (JCPDS No. 44-1481); (ii) peaks at 32.2° , 34.4° , and 41.2° were characteristic diffraction peaks of Ca_2SiO_4 (JCPDS No.49-1673); and (iii) peaks at 32.2° ,

TABLE 3: Comparison of the 15 wt.% Na_2CO_3 -CS-800 with recently reported heterogeneous catalysts.

Entry	Catalyst	Feedstock	Yield _f (%) ^a	Reuse times	Yield _r (%) ^b	Ref.
1	CaO	Commercial CaO	95.3	3	17.8	[58]
2	RM-500	Red mud	92.0	4	8.2	[41]
3	EFB-500	Oil palm empty fruit bunch	95.7	4	85.2	[59]
4	DW-Ni-700	Diaper waste, $\text{Ni}(\text{NO}_3)_2$	96.9	4	89.6	[40]
5	15 wt.% Na_2CO_3 -CS-800	CS	96.0	4	83.2	Present work

^aGC yield when the fresh catalyst was applied. ^bGC yield after the catalyst was recycled for several times.

FIGURE 14: Proposed mechanism for the 15 wt.% Na_2CO_3 -CS-800 catalyzed transesterification reaction of glycerol with DMC.

37.4°, 53.9°, 64.2°, 67.30°, 79.6°, and 88.6° were assigned to CaO (JCPDS No.48-1467) [53]. Figures 12(a) and 12(b) revealed that the crystalline phases of CS-800 before and after reuse had changed greatly, indicating the complete breakdown of crystalline structure of CS-800 after reuse. In contrast, the crystalline phases of the reused 15 wt.% Na_2CO_3 -CS-800 had little change after comparing Figure 12(c) with Figure 12(d). Besides, the diffraction peak for CaCO_3 in Figure 12(d) became obvious after reuse. Four weak diffraction peaks appeared at 18.0°, 28.9°, 33.9°, and 47.3°, which were ascribed to characteristic diffraction peaks of $\text{Ca}(\text{OH})_2$ as mentioned above. Moreover, the XRD patterns of the reused catalysts show the diffraction peaks of organics at low angles.

Figure 13 shows the FTIR spectra of the CS-800, the reused CS-800, the 15 wt.% Na_2CO_3 -CS-800, and the reused 15 wt.% Na_2CO_3 -CS-800. The spectrum of the reused CS-800 was very different from that of pristine CS-800. New peaks at 692 cm^{-1} , 875 cm^{-1} , and 1415 cm^{-1} were attributed to the typical vibration absorption of CO_3^{2-} [40, 55], indicating that the CO_2 in air might be absorbed and reacted with catalyst during cycling experiments. In the spectrum of pristine 15 wt.% Na_2CO_3 -CS-800, typical vibration absorption peaks of CO_3^{2-} are observed, meaning that the CaCO_3 generated during impregnation treatment still existed after calcination. Since crystal diffraction peaks of CaCO_3 in XRD are weak, it was reasonable to speculate that the CaCO_3 generated was in the form of amorphous state on the surface of

the catalyst particles. In the spectrum of reused 15 wt.% Na_2CO_3 -CS-800, typical vibration absorption peaks of CO_3^{2-} still existed. XRD results showed that the CaO in reused 15 wt.% Na_2CO_3 -CS-800 are well preserved. It clearly showed that the CaCO_3 contributed greatly to the stabilization of catalyst. The weak C-H stretching vibration peak at 2947 cm^{-1} was observed in the reused CS-800 and the 15 wt.% Na_2CO_3 -CS-800, which also proved the existence of organics on the reused catalyst. The broad absorption peak at 3416 cm^{-1} was attributed to the stretching vibration of O-H. The peak at 3642 cm^{-1} was ascribed to the O-H stretching vibration peak of $\text{Ca}(\text{OH})_2$.

XRD and FTIR investigation on the CS-800, the reused CS-800, the 15 wt.% Na_2CO_3 -CS-800, and the reused 15 wt.% Na_2CO_3 -CS-800 showed that there were some main factors leading to the deactivation of the catalyst. Firstly, leaching of CaO happened during the transesterification reaction of glycerol with DMC. Secondly, CaO reacted with H_2O and CO_2 in the environment to form $\text{Ca}(\text{OH})_2$ and CaCO_3 . Finally, the adhesion of organics also was one of the reasons that lead to the deactivation of catalyst. Moreover, we speculate that there were two main reasons for the catalyst to exhibit good stability and reusability after loading Na_2CO_3 . Firstly, more active Na_2O may be formed in the calcination process, which can preferentially react with H_2O and CO_2 in the environment and protect the active component CaO. Secondly, the uniformly dispersed amorphous CaCO_3 on CaO surface forms an insoluble masking shell on catalyst and slows down the leaching of CaO effectively.

3.8. Comparison of 15 wt.% Na_2CO_3 -CS-800 with Other Reported Heterogeneous Catalyst. Developing lost-cost, high-efficiency, and environmentally friendly heterogeneous catalyst is essentially important in the production of GC. Comparing the activity of the catalysts and feedstock, CS-based catalyst has a comparably high GC yield. Table 3 shows the recently reported heterogeneous catalysts and their catalytic ability [40, 41, 58, 59]. CaO and red mud could be directly used after simple calcination treatment. Their raw materials are bulky and readily available. Although they could give over 90% GC yield by fresh catalyst, the reuse capability is not satisfactory. The CaO gave only 17.8% GC yield after three cycles and the RM-500 gave only 8.2% GC yield after four cycles. The EFB-500 and DW-Ni-700 were prepared from waste materials. Although they showed high catalytic performances and reusability, lots of labor are needed to collect the waste materials. Moreover, thermal degradation of organic waste materials to prepare catalyst faced the problem of low catalyst yield, as well as smoke and dust emission, which is not environmentally friendly. Thus, the 15 wt.% Na_2CO_3 -CS-800 presents itself as a promising catalyst for the transesterification of glycerol with DMC by the merit of bulk availability and environmental friendliness.

3.9. Catalytic Mechanism of the 15 wt.% Na_2CO_3 -CS-800. The study results exhibited that the principal active components of the 15 wt.% Na_2CO_3 -CS-800 was CaO, which had

strong catalytic activity for the transesterification of glycerol with DMC. In addition to that, the CaCO_3 , which was generated during Na_2CO_3 solution impregnation with CS, also play a key role in preserving activity of catalyst. Based on the above phenomenon, the catalytic mechanism of the 15 wt.% Na_2CO_3 -CS-800 as heterogeneous solid base catalyst in the transesterification of glycerol with DMC was proposed, as shown in Figure 14. Firstly, glycerol contacted with the active sites on the surface of the 15 wt.% Na_2CO_3 -CS-800 in the form of hydrogen bonds, and then, glycerol was activated under the action of the active sites and thereby transformed into the active intermediate, namely, glyceroxide anion. Secondly, the active intermediate attacked DMC and reacted with DMC to form methyl glyceryl carbonate. At the same time, the methoxy group in DMC reacted with H^+ to form CH_3OH . Finally, with the further action of the active site of 15 wt.% Na_2CO_3 -CS-800, methyl glyceryl carbonate took place intramolecular nucleophilic reaction to generate GC and CH_3OH . The CaCO_3 , which is insoluble to all reactants and products, distributed on the surface of active CaO catalyst to form a shell. Although this shell could alleviate the leaching of CaO, it did not affect the mass transfer in the reaction process.

4. Conclusions

Solid base catalyst prepared by the impregnation-calcination method with Na_2CO_3 and CS as raw materials has excellent catalytic activity and reusability. The 15 wt.% Na_2CO_3 -CS-800 is the most suitable catalyst for the transesterification reaction of glycerol with DMC, and its main active component is CaO. When it was used in the transesterification reaction of glycerol with DMC, the optimized reaction conditions were as follows: reaction time of 90 mins, molar ratio of DMC-to-glycerol of 5:1, reaction temperature of 75°C , and catalyst dosage of 3 wt.%. Under these reaction conditions, glycerol conversion and GC yield were 98.1% and 96.0%, respectively. More importantly, the 15 wt.% Na_2CO_3 -CS-800 exhibited a good reusability in the transesterification reaction of glycerol with DMC. After five-time reuse, glycerol conversion and GC yield also remained above 80%. Therefore, the 15 wt.% Na_2CO_3 -CS-800 had excellent potential application in the transesterification of glycerol with DMC. Overall, our strategy has the following three advantages compared with the state-of-the-art works [40, 41, 44, 46]: (i) bulk availability of raw materials, no need to collect scattered waste to prepare catalyst; (ii) high yield of catalyst production, the thermal degradation of organic materials to prepare solid catalyst is faced with the problem of low catalyst yield, as well as smoke and dust emission, which is not environmentally friendly; and (iii) good reusability, the optimized catalyst can achieve 80.5% GC yield after five-time reuse, while the unmodified catalyst can only achieve 14.1% GC yield. In this study, waste CS is used to prepare catalyst, which can transform the worthless industrial waste into useful resources and realized the effective utilization of garbage resources. It not only helps to reduce the cost of waste treatment but also plays a role in protecting the environment.

Data Availability

The data (figures) that support the findings of this study are available upon request from the corresponding author.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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