Water glass derived catalyst for the synthesis of glycerol carbonate via the transesterification reaction between glycerol and dimethyl carbonate

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Abstract: Water glasses with different modulus (mole ratio of SiO$_2$ to Na$_2$O) were applied as a raw material to prepare five solid base catalysts for the synthesis of glycerol carbonate (GC) by the transesterification reaction between glycerol and dimethyl carbonate (DMC). The structure and properties of the five water glass-derived catalysts were investigated by XRD, FT-IR, FESEM, BET and acid–base titration methods. The catalysts with relatively low modulus, including 1.0, 1.5 and 2.0, presented good catalytic abilities, among which the catalyst derived from water glass with 2.0 modulus (WG-2.0) was chosen as the optimal catalyst in the synthesis of GC. This was because WG-2.0 showed the highest BET surface area, relatively high total basicity, and needed a less amount of NaOH during the preparation process. In the optimization experiments, this catalyst exhibited good catalytic ability with the glycerol conversion of 96.3 % and GC yield of 94.1 % under the condition of glycerol to DMC mole ratio of 1:4, WG-2.0 amount of 4 wt. %, reaction temperature of 348 K and reaction time of 90 min. Furthermore, the reusability experiment of WG-2.0 was also conducted and the results indicated that WG-2.0 could be reused five times without significant reduction in its catalytic ability.

Keywords: glycerol carbonate; glycerol; transesterification; water glass; catalyst.

INTRODUCTION

In recent years, the consumption of fossil fuel has been increasing rapidly with economic development around the world. This to a great degree has decreased the reserves of fossil fuel, which aroused great interests in seeking and developing new sources to satisfy the urgent demand for the fuel. To this end, biodiesel as a renewable fuel has been developed and become the best supplement for fossil fuel at the moment. However, the manufacture of biodiesel can produce a large amount of by-product, glycerol, which has brought about a neg-

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ative effect on the commercial development of biodiesel.\textsuperscript{2,3} Therefore, how to effectively use glycerol has aroused great attention in the field of chemical industry. To solve this problem, one of the meaningful methods was using glycerol to synthesize high value-added chemical products.\textsuperscript{4,5} A good case in point was using glycerol to synthesize glycerol carbonate (GC). Since GC has the advantages of low combustibility, good biodegradability, low toxicity, low water solubility, high viscosity and high boiling point, it has been used as a reaction solvent and emulsifier in the field of material synthesis. Thus, using glycerol formed during the manufacture of biodiesel to produce GC can not only help to solve the problem caused by the formation of a by-product, glycerol, in biodiesel industry but also generate reasonable profits.\textsuperscript{6,7}

In view of the methods developed for the synthesis of GC, the transesterification reaction between glycerol and dimethyl carbonate (DMC) is a much more efficient and environment-friendly method.\textsuperscript{8,9} As for this method, catalysts play an important role because they can increase the reaction rate and affect the selectivity of GC. In this regard, the effect of different basic and acid catalysts on the synthesis of GC by transesterification reaction had been investigated. The investigation results have shown that acid catalysts presented extremely poor catalytic ability, whereas base catalysts exhibited good catalytic ability with high glycerol conversion and GC yield.\textsuperscript{10,11} In this sense, considerable base catalysts have been developed in the transesterification reaction recently and their catalytic ability has also been investigated thoroughly.\textsuperscript{12,13} The homogeneous base catalysts such as K\textsubscript{2}CO\textsubscript{3} and NaOH showed good catalytic ability in the synthesis of GC, yet they were difficult to be separated from the product mixture. The heterogeneous catalysts such as metal oxide, supported inorganic salt, hydrotalcite, lipase, ionic liquid, etc. were easy to be separated from the product mixture. However, they exhibited such drawbacks as the leaching of active sites, poor reusability, costliness, and so on in the synthesis of GC by a transesterification reaction. For instance, although CaO as a typical heterogeneous basic metal oxide catalyst in the reaction showed excellent catalytic ability, the absorption of CO\textsubscript{2} on its surface led to the deactivation of CaO after several times reuse.\textsuperscript{14} The supported inorganic salt catalysts such as KF/Al\textsubscript{2}O\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}/MgO presented poor reusability in the reaction owing to the leaching of metal ions in these catalysts.\textsuperscript{15,16} The hydrotalcite (LDH) catalysts such as Ca/Al LDH needed rigorous reaction conditions, including the long reaction time and the high reaction temperature.\textsuperscript{17} Compared with the other heterogeneous catalysts mentioned above, the lipase catalysts exhibited good catalytic ability and reusability in the reaction; nevertheless their high preparation cost prohibited them from the large-scale industrial application.\textsuperscript{18} Therefore, it is necessary to seek inexpensive industrial materials to develop highly active, easily reusable and non-toxic heterogeneous catalysts.\textsuperscript{19}
Water glass (WG) is a basic industrial raw material. Due to its non-toxicity and high stability, WG has been used for producing glasses, ceramics, corrosion inhibitors, cleaning agents, molds, cement, and so on.\textsuperscript{20,21} Traditionally, WG was prepared by melting the mixture of $\text{Na}_2\text{CO}_3$ and $\text{SiO}_2$ at about 1674 K, followed by dissolving the liquid melt in water.\textsuperscript{22,23} This traditional method has two drawbacks. One is the need for high temperature which can lead to high energy consumption. The other is the consumption of $\text{Na}_2\text{CO}_3$ and $\text{SiO}_2$ which can result in the relatively high production cost of WG. In regard to these drawbacks, the methods of using industrial wastes as new resources to synthesize high-quality WG with low cost have been developed. For example, high-purity WG was prepared via a novel low-temperature co-melting reaction using slag from the acid leaching of coal-waste or gangue as the feedstock.\textsuperscript{23,24} Although the techniques to prepare high-quality WG have been developed at a fast pace, the application of WG is developing at a relatively slow pace.\textsuperscript{25} Thus, it is important to explore the possible applications of WG in new areas.

In this article, WG was first used to prepare base catalysts for the transesterification of glycerol with DMC to synthesize GC. The prepared WG derived base catalysts with different modulus were characterized by XRD, FT-IR, FESEM, BET and acid–base titration methods. The catalyst with the best performance was applied in the optimization of the transesterification of glycerol with DMC to synthesize GC. The effects of catalyst amount, mole ratio of glycerol to DMC, reaction time and reaction temperature on transesterification were studied. Moreover, the reusability of the catalyst was carefully evaluated.

**EXPERIMENTAL**

*Materials*

Glycerol (99.0 % purity), DMC (99.0 % purity), ethanol (99.7 % purity), and NaOH of analytical grades were purchased from Aladdin Chemical Co.. A commercial water glass with the modulus of 3.3 (31.5 % of $\text{SiO}_2$, 9.5 % of $\text{Na}_2\text{O}$) was bought from Tianjin Zhonghe Shengtai Chemical Co., Ltd., China.

*Catalyst preparation*

The water glass derived catalysts were prepared in two steps. In the first step, water glasses with different modulus were prepared by adding the appropriate amount of NaOH into the water glass with the modulus of 3.3, after which the mixture was sealed and stirred at 364 K for 30 min. The modulus of the resultant water glass was determined according to the literatures.\textsuperscript{26,27} In the second step, the water glasses with different modulus were dried up at 454 K for 120 min to remove the water. Then the obtained materials were heated up in a muffle furnace at 774 K for 240 min. After cooling to room temperature, the obtained materials were triturated and passed through a 120-mesh sieve to obtain the catalysts used in the transesterification reaction. The as-prepared catalyst was named as WG-m, where WG means the water glass and m means the corresponding modulus. For instance, the catalyst prepared by the water glass with the modulus of 2.0 was named as WG-2.0.
Characterization of the catalyst

The Brunauer–Emmet–Teller (BET) surface area of the catalysts was obtained by using a JW-BK122W instrument (JWGB, China). After the catalysts were degassed at 394 K for 180 min to remove the moisture on their surface before analysis, the nitrogen adsorption/desorption isotherms were measured at 77 K. The basic strength of the catalysts was determined by Hammett indicator method (see Supplementary material to this paper). The total basicity of the catalysts was measured by the titration method as described in the literature. X-ray diffraction (XRD) patterns of all the catalysts were obtained using a X. Pert Pro Mpo PW3040 (PANalytical B.V., Netherlands) instrument with CuKα radiation (λ = 0.1540 nm) at 40 kV and 30 mA. All the catalysts were examined at a scanning speed of 4° min⁻¹ in the 2θ range of 10–70°. The Fourier transform infrared (FT-IR) investigation of the catalysts was carried out on a Prestige-21 FTIR spectrometer (Shimadzu, Japan) from 400 to 2000 cm⁻¹ with the standard KBr disk method. The morphology observation of the catalysts was performed on a SU8010N (Hitachi, Japan) field emission scanning electron microscopy (FESEM) apparatus, operating at an accelerated voltage of 10 kV. Then, the catalysts were coated with a thin layer of golden alloy before observation.

Performance of the catalyst

The transesterification reaction was carried out in a 150 mL three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. In a typical reaction procedure, glycerol (4.6 g, 0.05 mol) and DMC (13.5 g, 0.15 mol) were charged into the flask, and the reaction mixture was heated up with stirring to 348 K. Then, the catalyst (0.09 g, 0.5 wt.% of the raw material) was added to the reaction mixture and reacted at 348 K for 90 min. After the reaction was finished, the catalyst was separated from the product mixture by filtration and a clear homogeneous solution was obtained. The product was analyzed by a GC-7890A gas chromatography instrument (Agilent, USA) equipped with a flame ionization detection (FID) using a Thermo TG-SQC capillary column (15 m×0.25 mm×0.25 μm). Tetraethylene glycol was used as the internal standard to calculate the glycerol conversion and GC yield (see Supplementary material to this paper).

RESULTS AND DISCUSSION

Catalyst characterization

The XRD patterns of the WG derived catalysts are depicted in Fig. 1. The characteristic peaks appearing at 16.8, 24.9, 29.3, 34.8, 37.2, 45.5, 48.1, 49.4, 52.1, 64.0 and 65.7° in Fig. 1a indicated that the main component of WG-1.0 was Na₂O·SiO₂ (JCPDS No.16-0818). With the increase of the WG modulus, obvious changes occurred to the diffraction patterns of the WG derived catalysts. The diffraction peaks observed at 23.6, 26.9, 27.8, 30.1, 33.8 and 36.6° in Fig. 1b showed the existence of α-Na₂O·2SiO₂ (JCPDS No.22-1397). Moreover, δ-Na₂O·2SiO₂ was also found in WG-1.5 due to the existence of the diffraction peaks appearing at 18.0, 23.5 and 37.1° (JCPDS No.22-1396). These results demonstrate that the crystalline phase of WG-1.5 was mainly composed of Na₂O·SiO₂, α-Na₂O·2SiO₂ and δ-Na₂O·2SiO₂. As to the diffraction pattern of WG-2.0 (Fig. 1c), only weak diffraction peaks were observed. Meanwhile, apart from the diffraction peaks
belonging to Na$_2$O·SiO$_2$, α-Na$_2$O·2SiO$_2$ and δ-Na$_2$O·2SiO$_2$, the characteristic peaks appearing at 15.0 and 21.5° indicated the existence of β-Na$_2$O·2SiO$_2$.\textsuperscript{32}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{XRD patterns of: a) WG-1.0, b) WG-1.5, c) WG-2.0, d) WG-2.5 and e) WG-3.0.}
\end{figure}

These results demonstrate that the crystallinity of WG-2.0 was lower than that of WG-1.0 and WG-1.5, and the crystalline phase of WG-2.0 was a composite of Na$_2$O·SiO$_2$, α-Na$_2$O·2SiO$_2$, β-Na$_2$O·2SiO$_2$ and δ-Na$_2$O·2SiO$_2$. With the continuous increase of the modulus of the WG derived catalysts, no diffraction peaks could be found in WG-2.5 and WG-3.0 (Fig. 1d and e), demonstrating that there was no ordered crystalline phase in WG-2.5 and WG-3.0. In addition, the XRD investigation results show that, with the increase of the modulus, the crystallinity of the WG derived catalysts kept decreasing till non-crystallizable materials formed in WG-2.5 and WG-3.0. This phenomenon resulted from the fact that, with the decrease of the content of Na$_2$O in the catalysts, more and more SiO$_4$ tetrahedra polymerized, leading to the formation of the silicate network and the destruction of the ordered structure in the WG derived catalysts.\textsuperscript{24,33}

FT-IR spectroscopy was applied to further investigate the structural features of the WG derived catalysts. As displayed in Fig. 2, the FT-IR spectra of the WG derived catalysts could be divided into two regions. One was above 1300 cm$^{-1}$, and the other was below 1300 cm$^{-1}$. In the region above 1300 cm$^{-1}$, the absorption band at about 1630 and 1440 cm$^{-1}$ was ascribed to the stretching vibration of the O–H group.\textsuperscript{34}

The FT-IR spectrum of WG-1.0 showed six characteristic bands appearing at about 520, 590, 710, 890, 970 and 1030 cm$^{-1}$, respectively. The band at 520 cm$^{-1}$
was ascribed to the bending vibration of Si–O. The band observed at 590 cm\(^{-1}\) corresponded to the vibration of the Si–O ring structure of the low polymerized SiO\(_4\) tetrahedra. The stretching vibration bands of Si–O–Si appeared at 710, 890 and 1030 cm\(^{-1}\). The stretching vibration band of Si–O–Na was found at 970 cm\(^{-1}\). With the increase of the modulus of WG to higher than 2.0, the band at 590 cm\(^{-1}\) could not be observed any more, indicating the disappearance of the ring structure of the low polymerized SiO\(_4\) tetrahedra. This was when the modulus of WG increased, because, the polymerization between SiO\(_4\) tetrahedra became more predominant and all the oxygen atoms around the Si atom were polymerized as the bridging oxygen atoms. This resulted in the formation of the Si–O network and the destruction of the Si–O ring structure. Moreover, the further polymerization of the SiO\(_4\) tetrahedra also led to the stretching vibration bands of Si–O–Si appearing at 710 and 890 cm\(^{-1}\) shifted to 780 and about 980 cm\(^{-1}\), respectively. During the polymerization process of SiO\(_4\) tetrahedra, the stretching vibration band of Si–O–Na was shifted to the higher wavenumber region due to the wrapping of Na\(^+\) in the crystal interior. However, this shift was overlapped with that of stretching vibration of Si–O–Si (from 890 to 980 cm\(^{-1}\)), leading to a broad band occurring between 1100–900 cm\(^{-1}\) (Fig. 2e). All these results demonstrate that the increase of the modulus of WG led to the change of the corresponding catalysts from a low polymerization state to a high polymerization state and the Si–O network structure formed in the catalysts with the modulus higher than 2.0.

![Fig. 2. FT-IR spectra of: a) WG-1.0, b) WG-1.5, c) WG-2.0, d) WG-2.5 and e) WG-3.0.](https://www.shd.org.rs/JSCS/)
The morphology of the WG derived catalysts was recorded by FESEM (Fig. 3). As observed in Fig. 3, these five catalysts, namely, WG-1.0, WG-1.5, WG-2.0, WG-2.5 and WG-3.0, showed different surface characteristics. WG-1.0 showed an irregular shape with considerable big holes on its uneven surface. The surface of WG-1.5 was much smoother than that of WG-1.0 and some irregular texture could be observed on its surface. As for WG-2.0, flake and spherical particles about 50 μm with smooth surface were found, which were frequently observed in silicate particles with the modulus of about 2.0, prepared by other methods. As far as WG-2.5 was concerned, near triangular-shaped partials with smooth surface were observed. In regard to WG-3.0, its surface was still much smoother than that of WG-1.0, although some irregularly shaped particles with holes on their surface were observed. The XRD, FTIR, and FESEM investigations showed the significant structural differences among the WG derived catalysts, which can greatly affect their properties.

Table I presents the BET, basicity and the catalytic ability of the WG derived catalysts. With the modulus of WG increasing from 1.02 to 3.02, the BET surface area of the WG derived catalysts increased at first and then decreased. The highest BET surface area of 6.2 m²·g⁻¹ was obtained in WG-2.0 with the modulus of 2.04, which may be due to its flake and spherical structures. The basic strength of the prepared WG derived catalysts decreased with the increase of the WG modulus. As observed in Table I, WG-1.0, WG-1.5 and WG-2.0 displayed the high basic strength of 15.0 < $H_\ast$ < 18.4. Comparatively, WG-2.5 and WG-3.0 exhibited low basic strength of 9.8 < $H_\ast$ < 15.0. Meanwhile, the total basicity of the WG derived catalysts exhibited a similar tendency. Among
the five catalysts, WG-1.0 had the highest total basicity of 23.1 mmol/g, whereas WG-3.0 had the lowest total basicity of 12.9 mmol/g. With the increase of the modulus of the WG derived catalysts, the content of Na$_2$O in them decreased, leading to the decrease of their basic strength and total basicity, which could affect their catalytic ability. To compare the catalytic ability of the WG derived catalysts, these catalysts were employed in the transesterification reaction between glycerol and DMC, and the result is also shown in Table I. When they were used under the same reaction condition, WG-2.5 and WG-3.0 exhibited relatively poor catalytic ability with the glycerol conversion of 72.1 and 67.3 %, and the GC yield of 70.2 and 65.8 % due to their relatively low basic strength and total basicity. In contrast, WG-1.0, WG-1.5 and WG-2.0 exhibited better catalytic ability with the glycerol conversion of higher than 91 %, and the GC yield of higher than 89 %. Although the total basicity of WG-2.0 was lower than that of WG-1.0, the BET surface area of WG-2.0 was much higher than that of WG-1.0. This was the reason why WG-2.0 presented similarly good catalytic ability as WG-1.0 in the reaction. Moreover, the consumption of sodium hydroxide to synthesize WG-2.0 was much less than that of sodium hydroxide to synthesize WG-1.0, which led to the lower preparation cost of WG-2.0. Thus, WG-2.0 is the most suitable catalyst among the WG derived catalysts for the transesterification between glycerol and DMC.

**TABLE I. Property comparison of the WG derived catalysts in the synthesis of GC**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Modulus of resultant WG</th>
<th>BET surface area, m$^2$/g$^1$</th>
<th>Base strength</th>
<th>Total basicity, mmol g$^{-1}$</th>
<th>Glycerol conversion$^a$, %</th>
<th>GC yield$^a$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>WG-1.0</td>
<td>1.02</td>
<td>2.2</td>
<td>$15.0 &lt; H_2 &lt; 18.4$</td>
<td>23.1</td>
<td>91.4</td>
<td>89.2</td>
</tr>
<tr>
<td>WG-1.5</td>
<td>1.51</td>
<td>2.5</td>
<td>$15.0 &lt; H_2 &lt; 18.4$</td>
<td>17.9</td>
<td>91.2</td>
<td>89.3</td>
</tr>
<tr>
<td>WG-2.0</td>
<td>2.04</td>
<td>6.2</td>
<td>$15.0 &lt; H_2 &lt; 18.4$</td>
<td>16.4</td>
<td>91.3</td>
<td>89.1</td>
</tr>
<tr>
<td>WG-2.5</td>
<td>2.48</td>
<td>3.4</td>
<td>$9.8 &lt; H_2 &lt; 15.0$</td>
<td>14.8</td>
<td>72.1</td>
<td>70.2</td>
</tr>
<tr>
<td>WG-3.0</td>
<td>3.03</td>
<td>2.8</td>
<td>$9.8 &lt; H_2 &lt; 15.0$</td>
<td>12.9</td>
<td>67.3</td>
<td>65.8</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: glycerol: 0.05 mol (4.6 g), DMC: 0.15 mol (13.5 g), catalyst: 0.09 g (0.5wt. %), temperature: 348 K, time: 90 min

**Effect of reaction conditions**

Catalyst amount can greatly affect the reaction rate. This is because catalyst amount is closely related to the concentration of active site that glycerol molecule needs to react with DMC and form GC. The influence of catalyst amount on the catalytic ability of WG-2.0 in the transesterification reaction is presented in Fig.4a. A steady rising tendency occurred to the conversion of glycerol with the increase of the amount of WG-2.0 from 1 to 4 wt. %. The highest glycerol conversion of 93.2 % and GC yield of 90.1 % was obtained when the amount of WG-2.0 was 4 wt. %. With further addition of the catalyst amount from 4 wt. % to 5 wt. %, no obvious enhancement of the glycerol conversion of and GC yield...
could be observed. Thus, 4 wt. % is the optimal catalyst amount of WG-2.0 for the transesterification reaction.

![Graph a] Fig. 4. a) Effect of catalyst amount on the transesterification of glycerol with DMC; b) effect of glycerol to DMC molar ratio on the transesterification of glycerol with DMC; c) effect of reaction temperature on the transesterification of glycerol with DMC; d) effect of reaction time on the transesterification of glycerol with DMC.

The influence of the molar ratio of glycerol to DMC on glycerol conversion and GC yield is depicted in Fig. 4b. The conversion of glycerol rose steadily with the mole ratio of glycerol to DMC changed from 1:1 to 1:4. This was caused by the fact that excessive DMC can promote the shift of reaction equilibrium to the product side. With the continuous increase of DMC, the glycerol conversion and GC yield increased subsequently. The maximum glycerol conversion of 95.1 % and GC yield of 92.2 % were achieved at the mole ratio glycerol to DMC of 1:4. However, when the molar ratio of glycerol to DMC was higher than 1:4, no obvious increase in the glycerol conversion emerged. Therefore, 1:4 is the optimal mole ratio of glycerol to DMC for the transesterification reaction.

The effect of reaction temperature on glycerol conversion and GC yield is presented in Fig. 4c. The glycerol conversion increased with the reaction tempe-
rature increasing from 333 to 353 K. This was because the increase of reaction temperature enhanced the probability of the molecular collision that could lead to the rise of the reaction rate. A maximum glycerol conversion of 96.3 % was achieved when the reaction temperature was at 348 K, suggesting that the increase in reaction temperature resulted in the rise of the transesterification reaction rate, which in turns enhanced the conversion of glycerol. Therefore, 348 K is the optimum reaction temperature for the transesterification of glycerol with DMC.

Sufficient reaction time can promise high glycerol conversion. The effect of reaction time on the transesterification reaction of glycerol with DMC is presented in Fig. 4d. The conversion of glycerol to GC increased with the reaction time increasing from 30 to 90 min. The maximum of glycerol conversion of 96.3 % was reached when the transesterification operated for 90 min and remained almost at the same level when the reaction continued for 150 min. The above results demonstrate that 90 min was sufficient for obtaining the maximum catalytic performance with high glycerol conversion and GC yield.

Catalyst reusability

The reusability of catalysts is an important character for evaluating its catalytic performance. According to the above optimal experiment results, the experiment with reused WG-2.0 was carried out. The reusability of WG-2.0 is shown in Fig. 5. When the fresh WG-2.0 was used in the reaction, the glycerol conversion of 96.3 % and GC yield of 94.1 % were achieved. After the reaction was finished, WG-2.0 was separated from the produce mixture by filtration method.

The separated WG-2.0 was washed with ethanol to remove the adsorbed organic compounds and dried in the oven at 474 K for 120 min for the next ran. In the first cycle, WG-2.0 still showed the high glycerol conversion of 96.0 % and GC yield of 93.7 %. In the subsequent four cycles, although less than 3 % decrease of the glycerol conversion and GC yield occurred, the catalytic ability
of the reused WG-2.0 remained at the high level after four times reuse, indicating the good stability and reusability of WG-2.0. Moreover, the structure of the catalyst hardly changed after five times reuse (Figs. S1 and S2 of the Supplementary material). Therefore, WG-2.0 was a stable catalyst for the transesterification of glycerol with DMC.

Comparison of the catalytic activity of different catalysts

The prepared optimal catalyst WG-2.0 was compared with the reported inorganic catalysts applied in the transesterification of glycerol with DMC, namely CaO, CeO$_2$/CdO, Li/ZnO and Ca/Al LDH. The results are presented in Table II. When CaO, CeO$_2$/CdO, Li/ZnO, Ca/Al LDH and WG-2.0 were used in the reaction for the first time, they all showed high glycerol conversion in the synthesis of GC, namely 91.2, 91.0, 97.6, 97.0 and 96.3 %. However, after four times reuse, a sharp decrease in the catalytic ability of the reused CaO appeared, with the glycerol conversion decreasing from 91.2 to 53.2 %. This was attributed to the fact that CaO adsorbed CO$_2$ and water in the environment formed CaCO$_3$ and Ca(OH)$_2$. Similar situation happened to CeO$_2$/CdO, Li/ZnO and Ca/Al LDH. When they were used in the reaction for four or five times, they exhibited poor catalytic ability with relatively low glycerol conversion (80.5, 66.6 and 84.0 %) due to the dissolving of their active site. Compared with these catalysts, the high catalytic ability of WG-2.0 prepared in this study remained, with the glycerol conversion of higher than 94 % after five times reuse, demonstrating that WG-2.0 was a promising catalyst in the synthesis of GC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Glycerol conversion catalyzed by the fresh catalyst, %</th>
<th>Number of reuse</th>
<th>Glycerol conversion catalyzed by the reused catalyst, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CaO</td>
<td>91.2</td>
<td>4</td>
<td>53.2</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>CeO$_2$/CdO</td>
<td>91.0</td>
<td>5</td>
<td>80.5</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Li/ZnO</td>
<td>97.6</td>
<td>4</td>
<td>66.6</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>Ca/Al LDH</td>
<td>97.0</td>
<td>4</td>
<td>84.0</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>WG-2.0</td>
<td>96.3</td>
<td>5</td>
<td>94.0</td>
<td>Present work</td>
</tr>
</tbody>
</table>

CONCLUSION

The WG derived catalysts with different modulus were prepared and first used in the transesterification of glycerol with DMC. WG-2.0, which was composed of Na$_2$O·SiO$_2$, $\alpha$-Na$_2$O·2SiO$_2$, $\beta$-Na$_2$O·2SiO$_2$ and $\delta$-Na$_2$O·2SiO$_2$, was superior to the other WG derived catalysts. It had the characteristics of a relative high BET surface area and total basicity, low preparation cost and good catalytic activity. In this regard, WG-2.0 was chosen as the optimal catalyst in the synthesis of GC. The high glycerol conversion of 96.3 % and GC yield of 94.1 % could be achieved.
under the optimum reaction conditions: DMC to glycerol mole ratio of 4:1, reaction temperature of 348 K, reaction time of 90 min and WG-2.0 catalyst amount of 4 wt. %. Moreover, WG-2.0 also exhibited excellent stability with the glycerol conversion decreasing less than 3 % even after five times reuse. Therefore, WG-2.0 not only has the potential industrial application in the synthesis of GC, but also greatly inspires the exploration of WG in the field of catalysis.

SUPPLEMENTARY MATERIAL

Additional experimental data are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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