Microwave assisted rapid synthesis of glycerol carbonate from glycerol catalyzed by anhydrous sodium silicate

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Abstract. Glycerol carbonate, a value-added derivative of biomass glycerol, has been synthesized by the transesterification of dimethyl carbonate with glycerol using anhydrous sodium silicate (Na$_2$SiO$_3$) as highly efficient, green and available solid base catalyst. The yield of glycerol carbonate reached up to 93% in 10 minutes under microwave irradiation. The result of leaching test indicated Na$_2$SiO$_3$ was a well-defined heterogeneous catalyst for the reaction. In addition, Na$_2$SiO$_3$ could be reused in 4 runs without significant loss of its catalytic activity.

1. Introduction
During the production of biodiesel, the amount of glycerol is about one tenth of biodiesel. Transformation of glycerol has attracted much attention since biodiesel production increased annually at high speed. Glycerol can be converted into several value-added chemicals, such as 1,3-propanediol, propylene glycol, acrolein and epichlorohydrin [1]. One of the most attractive derivatives of glycerol is glycerol carbonate (GC) which has been widely used as green solvent, surfactant and electrolyte. GC is also an important chemical intermediate for the synthesis of glycidol, polycarbonate and polyurethane [2].

Several routes have been reported for the phosgene-free synthesis of GC from glycerol. Among them, the transesterification of dimethyl carbonate (DMC) with glycerol is one of most important methods because of nontoxic raw materials, high yield and mild reaction conditions. This reaction has been carried out in the presence of homogeneous base catalyst, such as KOH, NaOH, K$_2$CO$_3$ and Na$_2$CO$_3$, et al. However, the separation of homogeneous catalyst from product is difficult. Enormous energy will be consumed in the distillation separation because of high boiling point of GC (353.9°C at atmosphere). According to the requirement of green and sustainable chemistry, the development of heterogeneous catalyst is necessary. Ochoa-Gómez, et al firstly screened different acid and base heterogeneous catalysts for the synthesis of GC [3]. Among investigated heterogeneous catalyst, the catalytic activity followed the order of basic strength of these materials, and CaO which was calcined at 900°C performed the best catalytic property. However, the activity of CaO decreased dramatically after the first recycle. Mg/Al/Zr mixed oxide base catalysts were prepared and evaluated for the synthesis of GC from DMC and glycerol without solvent by Malyaadri, et al [4]. The result showed that Mg/Al/Zr mixed oxide exhibited higher activity than Mg-Al hydroxalcite. Reusability test of Mg/Al/Zr mixed oxide was not listed. Bai, et al found that the catalytic performance of KF modified hydroxyapatite was comparable to the homogeneous catalyst of KF [5]. But the loss of KF was inevitable. Thus, it is still interesting and challenging to develop highly efficient heterogeneous catalyst for GC synthesis [6].
Anhydrous sodium silicate (Na$_2$SiO$_3$) prepared by facile calcination of commercial Na$_2$SiO$_3$·9H$_2$O was a green, cheap and efficient solid base catalyst for the production of biodiesel. Herein, high yield of GC was obtained from DMC and glycerol using Na$_2$SiO$_3$ as reusable heterogeneous catalyst under mild reaction conditions. In addition, we found that microwave irradiation can accelerate the reaction remarkably.

2. Experimental

2.1. Catalyst preparation and characterization
According to the TG-DTA curves of Na$_2$SiO$_3$·9H$_2$O, crystal water of Na$_2$SiO$_3$·9H$_2$O could be completely removed at 200°C in 1 h. Herein, Na$_2$SiO$_3$ was prepared by the simple calcination of commercial Na$_2$SiO$_3$·9H$_2$O under air atmosphere within 2 h at 200°C, 300°C and 400°C, respectively (denoted as Na$_2$SiO$_3$-200, Na$_2$SiO$_3$-300 and Na$_2$SiO$_3$-400). As-calcined massive Na$_2$SiO$_3$ was sieved to 80 mesh before using it as catalyst for GC synthesis. FT-IR spectra of Na$_2$SiO$_3$ were obtained by Nicolet 560 in KBr pellets.

2.2. Catalytic reactions
Typical procedure for the synthesis of GC: 4.60 g (50 mmol) glycerol, 13.50 g (150 mmol) DMC and 0.065 g (1 mol%, based on glycerol) Na$_2$SiO$_3$ were charged into a 50 mL flask equipped with a magnetic stirring and a reflux condenser. The reaction mixture was then heated by microwave irradiation (power: 240 W) with continuous stirring. Timing begins with appearing reflux phenomenon. After 10 min, the mixture was cooled to room temperature. Solid catalyst was separated from product by filtration. And the product analyzed by gas chromatograph (Shandong Lunan Ruihong Co. SP-6890). The structure of the product was defined by GC-MS (HP 6890/5973). In the experiment to test the reusability of catalyst, Na$_2$SiO$_3$ was separated by filtration, and directly reused for the next run.

3. Results and discussion

3.1. Characterization of catalyst
FT-IR spectra of Na$_2$SiO$_3$·9H$_2$O and Na$_2$SiO$_3$ (prepared by calcination of Na$_2$SiO$_3$·9H$_2$O at 200°C in 2 h) was shown in Figure 1. Their spectra revealed a significant decrease for the intensity of water peak (centered at ~3400 and 3490 cm$^{-1}$, respectively). It indicated that most of absorbed water has been removed after calcination. In addition, the spectra of Na$_2$SiO$_3$·9H$_2$O showed an absorption band at ~1000 cm$^{-1}$ corresponding to the stretching vibration of Si-O-Na or Si-O (terminal oxygen). In comparison with Na$_2$SiO$_3$·9H$_2$O, intensity of Si-O-Na stretching peak of Na$_2$SiO$_3$ was weakened along with a high wavenumber shift. It means the number of Si-O-Na bond was reduced, resulting by the polymerization of SiO$_4^{2-}$ structural unit.

![Figure 1. FT-IR spectra of Na$_2$SiO$_3$·200 (UP) and Na$_2$SiO$_3$·9H$_2$O (Bottom).](image-url)
3.2. Catalytic performance

It was well known that the transesterification of DMC with glycerol is thermodynamically favourable for GC synthesis. High yield of GC could be obtained from DMC and glycerol using a base as catalyst. However, GC was almost not detected without catalyst (Entry 1), which was agreed well with results reported by literatures. When anhydrous Na$_2$SiO$_3$ prepared by calcination of Na$_2$SiO$_3$·9H$_2$O at 200°C (denoted as Na$_2$SiO$_3$-200) was used as catalyst, about 93% yield of GC was obtained with 98% selectivity at 75°C in 0.5 h (Entry 2). Detected by GC-MS, the main by-product was glycidol forming by the decarboxylation of GC.

Effect of calcination temperature on the synthesis of GC was also investigated. As shown in Table 1, the yield of GC has no remarkable change with increasing the calcination temperature from 200°C to 400°C (Entry 2-4). The basicity of above anhydrous Na$_2$SiO$_3$ was tested since the basicity of catalysts was one of the key factors influencing their catalytic property for GC synthesis. Although basicity distributions of Na$_2$SiO$_3$-200, Na$_2$SiO$_3$-300 and Na$_2$SiO$_3$-400 were different, their total basicity was close to each other. It means that the activity of anhydrous Na$_2$SiO$_3$ for GC synthesis might depend on its total basicity.

Table 1 Catalytic property of various catalysts for the transesterification of DMC with glycerol

| Entry | Catalyst       | Amount of catalyst (%) | Reaction time (h) | Conversion (%) | Selectivity of GC (%) |
|-------|----------------|------------------------|-------------------|----------------|-----------------------|
| 1     | -              | -                      | 0.5               | -              | -                     |
| 2     | Na$_2$SiO$_3$-200 | 1.6                    | 0.5               | 93             | 98                    |
| 3     | Na$_2$SiO$_3$-300 | 1.6                    | 0.5               | 93             | 98                    |
| 4     | Na$_2$SiO$_3$-400 | 1.6                    | 0.5               | 92             | 98                    |
| 5     | Na$_2$SiO$_3$·9H$_2$O | 1.6             | 0.5               | 73             | 97                    |
| 6     | NaOH           | 1.6                    | 0.5               | 98             | 99                    |

a Reaction conditions: Glycerol (4.60 g, 50 mmol), DMC (13.50 g, 150 mmol), 90°C.
b Molar ratio of catalyst to glycerol.
c Determined by gas chromatograph.

Comparing with anhydrous Na$_2$SiO$_3$, Na$_2$SiO$_3$·9H$_2$O performed a lower activity for the transesterification of DMC with glycerol (Entry 5). As the existence of crystal water, ortho silicate (H$_4$SiO$_4$) and sodium hydroxide (NaOH) were produced by the partial hydrolysis of Na$_2$SiO$_3$·9H$_2$O. Among them, the catalytic activity of homogeneous NaOH was slightly higher than that of anhydrous Na$_2$SiO$_3$ (Entry 6). However, solid catalyst obviously adhered to the bottom of reactor because of the produce of viscous H$_4$SiO$_4$, resulting the difficult of mass transfer. It might be one of reasons for the relatively low activity of Na$_2$SiO$_3$·9H$_2$O. As a result, Na$_2$SiO$_3$-200 was selected as the optimal catalyst for the transesterification of DMC with glycerol.

3.3. Leaching test

A hot leaching test was performed to investigate whether the transesterification of DMC with glycerol takes place homogeneously or heterogeneously, and the result was summarized in Figure 2. As the reaction completed too quickly under microwave irradiation, leaching test was carried out under conventional heating (oil bath). After removing the catalyst by filtration at 10 min, the yield of GC had no viewable change in the filtrated solution even prolonging the reaction time to 40 min. It indicated that the anhydrous Na$_2$SiO$_3$ is a well-defined heterogeneous catalyst for the transesterification of DMC with glycerol.
Figure 2. Leaching test for Na$_2$SiO$_3$ in the transesterification of DMC with glycerol
Reaction conditions: Glycerol (4.60 g, 50 mmol), DMC (13.50 g, 150 mmol), Na$_2$SiO$_3$-200 (1.0%, based on glycerol), 90°C.

3.4. Reusability of catalyst
The reusability of anhydrous Na$_2$SiO$_3$ was also examined for the synthesis of GC from DMC and glycerol. After the completion of the reaction, the catalyst was filtered and directly used for the next time. As shown in Table 2, Na$_2$SiO$_3$ could be reused for the transesterification of DMC with glycerol in 4 runs with only slight loss of its catalytic activity, indicating that Na$_2$SiO$_3$ performed well reusability. It was reported a dramatic loss of CaO activity in the transesterification because of carbonation and hydration resulting by air exposure during short time (3 min). According to the results, Na$_2$SiO$_3$ exhibited relatively higher stability than CaO with air exposure. Certainly, Na$_2$SiO$_3$ also could not keep stable after exposing to air for a long time. However, the activity of catalyst could almost recover after simple calcination at 200°C.

Table 2. Reusability of anhydrous Na$_2$SiO$_3$ for GC synthesis $^a$

| Run       | Yield (%) |
|-----------|-----------|
| 1         | 93        |
| 2         | 92        |
| 3         | 93        |
| 4         | 91        |
| 5 (air exposure) $^b$ | 72        |
| 5 (calcination) $^c$ | 91        |

$^a$ Reaction conditions: Glycerol (4.60 g, 50 mmol), DMC (13.50 g, 150 mmol), Na$_2$SiO$_3$-200 (1.0%, based on glycerol), microwave irradiation power (240 W), 10 min.

$^b$ Na$_2$SiO$_3$ (after 4 time run) exposed to air for 5 h.

$^c$ Na$_2$SiO$_3$ (after 4 time run) exposed to air for 5 h, and calcined at 200°C for 2 h.

4. Results and discussion
Anhydrous Na$_2$SiO$_3$ is an efficient, green, cheap and available heterogeneous catalyst for the transesterification of DMC with glycerol to synthesis GC. It can be prepared by the simple calcination of commercial Na$_2$SiO$_3$·9H$_2$O at relative low temperature (200°C). This reaction can be obviously accelerated by microwave irradiation. Under optimal reaction conditions, GC yield reaches over 90% in less than 10 minutes using only 1% Na$_2$SiO$_3$ as catalyst. Moreover, anhydrous Na$_2$SiO$_3$ performed good reusability for the synthesis of GC.

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