



Microwave-assisted transesterification of glycerol with dimethyl carbonate over sodium silicate catalyst in the sealed reaction system

Song Wang*, Lanlan Xu, Patrick U. Okoye, Sanxi Li, Chengcheng Tian

School of Science, Shenyang University of Technology, Shenyang 110870, Liaoning, China

ARTICLE INFO

Keywords:

Transesterification
Glycerol carbonate
Microwave irradiation mode
Sodium silicate

ABSTRACT

Microwave-assisted transesterification of glycerol to glycerol carbonate (GC) using calcined sodium silicate (Na_2SiO_3) as a catalyst in the sealed reaction system was studied in this work. Effects of the parameters, including the molar ratio of dimethyl carbonate (DMC) to glycerol, the reaction temperature, the amount of the catalyst, the reaction time and, especially, the microwave-assisted reaction modes on glycerol conversion and GC yield were carefully investigated. It was found that the microwave-assisted reaction modes, namely, the temperature constant mode (TCM) and the power constant mode (PCM), greatly influenced the reaction. When the reaction was conducted in TCM, with the catalyst amount of 5 wt%, reaction temperature of 95 °C, DMC-to-glycerol molar ratio of 4:1, and reaction time of 15 min, the glycerol conversion and the GC yield reached 96.7% and 94.3%, respectively. Similar glycerol conversion and GC yield were also obtained under the condition of the catalyst amount of 1 wt%, DMC-to-glycerol molar ratio of 4:1, microwave irradiation input power of 175 W and reaction time of 50 s in PCM. The reaction in PCM showed much more advantages in reducing the amount of the catalyst and shortening the reaction time than that in TCM. Meanwhile, the transesterification of glycerol with DMC in PCM catalyzed by Na_2SiO_3 exhibited much higher reaction rate than that catalyzed by CaO. Moreover, in terms of the reaction in PCM, energy consumption could be reduced with the increase of the irradiation power. The investigation on the reusability of the Na_2SiO_3 catalyst in PCM showed that this catalyst could be reused in five reaction cycles without significant deactivation.

1. Introduction

To minimize the dependence of energy consumption on fossil fuels, biodiesel has been rapidly developed in the last decade. However, large-scale biodiesel manufacturing has produced a great amount of glycerol as a by-product [1,2]. With the accumulation of biodiesel glycerol waste, the question of how to transform glycerol into high-value-added derivatives has drawn great attention in the field of biodiesel industry [3–6].

Glycerol carbonate (GC) is an important glycerol derivative. It has good biodegradability, low flammability, low viscosity, low toxicity, water solubility and high boiling point [7–9]. GC is also an important intermediate to produce phosgene-free polycarbonates and isocyanate-free polyurethanes [10,11]. Currently, some methods have been widely used to obtain GC, namely, the phosgenation of glycerol [12], the direct carbonylation of glycerol with carbon dioxide [13,14], the glycerolysis of urea [15–17], and the transesterification of glycerol with dimethyl carbonate (DMC) [18–21], etc. Among these methods, the transesterification of glycerol with DMC is more efficient than others for

obtaining GC under relatively mild conditions.

However, there are two important factors that need to be optimized in the transesterification of glycerol with DMC. One is to prepare an efficient catalyst. Recent studies have reported comprehensive catalysts, such as base and enzymes [22–27]. However, these reported catalysts showed drawbacks, namely, poor reusability, relatively high toxicity, complex preparation procedure, and high cost. In this regard, it is necessary to develop a cheap, recyclable, and highly active catalyst that can be used under mild and solvent-free conditions. As a strongly basic compound, sodium silicate (Na_2SiO_3) is an efficient catalyst in transesterification reactions, and it can be easily obtained and reused at industrial scale [28,29].

The other is to improve energy efficiency during the preparation process. Taking high energy consumption of the conventional-heating method into account, various studies have been conducted on developing process intensification technologies based on ultrasound and microwave irradiation [30,31]. The microwave-assisted preparation shows many advantages, such as reduction of reaction time and absence of noise. Therefore, it has been used as a non-conventional preparation

* Corresponding author.

E-mail address: wangsong@sut.edu.cn (S. Wang).

method for the transesterification of glycerol with DMC [32–34]. However, these reported microwave-assisted transesterification reactions of glycerol with DMC were mainly carried out in open reaction systems and in the temperature constant mode (TCM). Here, the TCM refers to the mode in which the reaction system is always maintained at a constant reaction temperature by applying low microwave irradiation power (lower than 50 W) after an initial application of high microwave irradiation power (higher than 500 W) for no more than 1 min. It is worth noting that reactions carried out in open systems and in TCM bring about two problems. One is the volatilization of methanol. Investigations have shown that the presence of methanol in the open reaction system exerts a positive effect because it can enhance the miscibility between DMC and glycerol [35]. However, this beneficial effect is eliminated by the occurrence of methanol volatilization, which also pollutes the environment. The other is the extension of the reaction time in TCM. In the transesterification of glycerol with DMC, glycerol is a good absorber of microwave radiation. When microwave irradiation is used in the reaction it can directly excite the glycerol molecule through energy transfer occurring in less than a nanosecond, which can result in a high instantaneous temperature of the glycerol molecule [36]. The higher microwave irradiation power can lead to a higher and more consistent instantaneous temperature, which can greatly accelerate the reaction rate and reduce the reaction time [37]. However, in the reported TCM process, the microwave irradiation power was always maintained at a very low value to maintain a constant reaction temperature during the reaction, and the high-power microwave irradiation was only applied at the initial stage of the reaction. Thus, to date, little has been investigated on the advantages of the microwave irradiation with a constant high power in the transesterification of glycerol with DMC.

The present study investigated the microwave-assisted transesterification of glycerol with DMC over the Na_2SiO_3 catalyst in the sealed reaction system. Firstly, the effect of the microwave-assisted reaction condition on the Na_2SiO_3 catalyzed transesterification of glycerol with DMC was elucidated. Secondly, the catalytic abilities of Na_2SiO_3 in two microwave-assisted reaction modes, namely, the temperature constant mode (TCM) and the power constant mode (PCM), were compared with the CaO catalyst. At last, energy consumption in the Na_2SiO_3 catalyzed microwave-assisted transesterification of glycerol with DMC was studied.

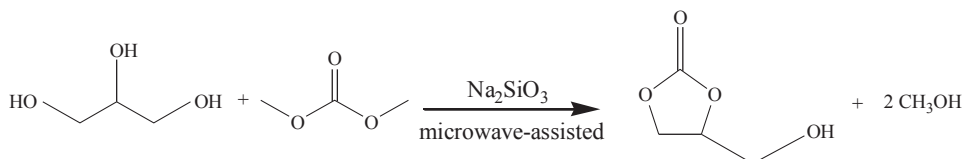
2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade and used without further purification. DMC, glycerol, sodium silicate (19.3–22.8 wt% of Na_2O) and CaO were obtained from Damao Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Catalyst preparation

The Na_2SiO_3 catalyst was prepared by calcination and sieving as reported previously [29]. Firstly, Na_2SiO_3 was heated in an oven at a rate of $10^\circ\text{C min}^{-1}$ from room temperature to 200°C and calcined for 2 h. Then the calcined Na_2SiO_3 was triturated and passed through a 120-mesh sieve. The obtained calcined Na_2SiO_3 was used as the catalyst in the transesterification of glycerol with DMC.



Scheme 1. Microwave-assisted transesterification of glycerol with DMC.

To prepare the CaO catalyst, CaO was heated in an oven at a rate of $10^\circ\text{C min}^{-1}$ from room temperature to 900°C and calcined for 2 h. Then the calcined CaO was triturated and passed through a 120-mesh sieve.

2.3. Catalyst characterization

The measurement of X-ray diffraction (XRD) was conducted by a X. Pert Pro Mpo PW3040 (PANalytical B.V., Netherlands) using $\text{CuK}\alpha$ radiation ($\lambda = 0.1540\text{ nm}$) at 40 kV and 30 mA. Catalyst samples were scanned in the 2θ range of $5\text{--}80^\circ$ at a scanning speed of 4° min^{-1} . A Prestige-21 (Shimadzu, Japan) FT-IR spectrometer was used to record Fourier transform infrared spectra (FT-IR) of the catalysts using the standard KBr disk method. The spectra were recorded in the region of $4000\text{--}400\text{ cm}^{-1}$. A TGA Q50 (TA, US) was used to perform the thermogravimetric analysis (TGA) under nitrogen atmosphere at the heating rate of $10^\circ\text{C min}^{-1}$ from 50°C to 800°C . The basic properties of the catalysts were determined by the Hammett indicator method as described in literatures [38,39]. A TSQ 8000 Evo Triple Quadrupole GC-MS/MS (Thermo Fisher Scientific, USA), equipped with a Thermo TG-SQC capillary column ($15\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$), was applied to conduct the gas chromatography-mass spectrometry analysis. The chemical composition of the catalysts was investigated using a Phenom Pro X scanning electron microscope (Philips, Netherlands) equipped with energy-dispersive spectroscopy (EDS). The leaching of the catalyst active site was investigated via EDS.

2.4. Microwave-assisted transesterification

The microwave-assisted transesterification of glycerol with DMC to produce GC was carried out in a Monowave 400 microwave reactor (Anton Paar, Austria) equipped with an infrared temperature sensor, a sealable glass vessel, an electromagnetic stirrer, a magnetron delivering continuous microwave irradiation power, and a sealing system. For the sake of safety, the reaction system was controlled below 200°C and 10 bar, respectively. The microwave-assisted transesterification of glycerol with DMC is illustrated in Scheme 1.

In a typical experiment, glycerol (0.92 g, 0.01 mol) and DMC (3.6 g, 0.04 mol) were successively charged into a 30 mL glass vessel and mixed with the Na_2SiO_3 catalyst (0.23 g, 5 wt% of raw material). The glass vessel was sealed with a snap cap and placed into the reactor. When the reaction was carried out in TCM, the reaction mixture was heated to 95°C in thirty seconds and maintained for 15 min. When the reaction was carried out in PCM, the reaction mixture was subjected to microwave irradiation with a constant power of 175 W for ten seconds. After the reaction mixture was cooled to room temperature, microwave irradiation of 175 W was again applied for ten seconds. These operations were repeated five times until the reaction was finished. After the reaction, the catalyst was isolated by filtration from the product mixture, and a transparent homogeneous solution was obtained. The product was analyzed by a GC-7890A gas chromatography (Agilent, US) equipped with flame ionization detection (FID) using a Thermo TG-SQC capillary column ($15\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Cumene was used as the internal standard. Based on the assumption that glycerol is the limiting reactant, glycerol conversion, GC yield and GC selectivity were calculated as described in literatures [29,33]. The turnover frequency (TOF) of the catalyst was calculated according to the method proposed in literatures [40,41].

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